Thesis Report

On

PHASE TRANSFER CATALYZED SYNTHESIS OF BIS (4-CHLOROBENZYL) SULFIDE USING HYDROGEN SULFIDE

In partial fulfillment for the award of the Degree of

Master of Technology

In

Chemical Engineering

Submitted by

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NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA

CERTIFICATE

This is to certify that the project entitled "PHASE TRANSFER CATALYZED SYNTHESIS OF BIS(4-CHLOROBENZYL) SULFIDE USING HYDROGEN SULFIDE**"** submitted by **Devipriya Gogoi** (213CH1117) in partial fulfilment of the requirements for the award of Master of Technology degree in Chemical engineering, Department of Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge the matter embodied in this thesis has not been submitted to any other university/Institute for the award of any Degree.

Date: 25.05.2015

Place: Rourkela

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ABSTRACT

The present research work is oriented towards a green technology that utilizes the environmentally hazardous chemicals like hydrogen sulfide (H_2S) and to synthesize commercially important chemicals to overcome the disposal problems as well as to improve the economy of the process. This proposed work involves two stages: firstly, selective absorption of H_2S in aqueous alkanolamine solution likes Methyl-diethanolamine (MDEA) and then the reaction of this H_2S-rich MDEA with the organic compound. The overall objectives are to synthesize the aromatic thioether like bis(4-chlorobenzyl) sulfide using hydrogen sulfide rich aqueous MDEA solution and 4-chlorobenzyl chloride (CBC). 4-chlorobenzyl mercaptan (CBM) was identified from the reaction mixture as a secondary product. The biphasic reactions were performed in a batch reactor using a phosphonium based phase transfer catalyst, Ethyltriphenyl phosphonium bromide because of its thermal stability. In this system, we developed the alternative to the expensive Claus process for utilization of hydrogen sulfide to produce commercially significant value added chemicals. The role of various phases such as agitation speed, catalyst concentration, temperature variation, sulfide concentration, MDEA concentration and reactant concentration in enhancing the selectivity towards bis(4-chlorobenzyl) sulfide has been investigated. The apparent activation energy was found to be 11.28 kJ/mol that emphases the reaction to be a kinetically controlled reaction. The experiments show encouraging results with 87.57% conversion of reactant 4-chlorobenzyl chloride and 89.48% selectivity of the desired product bis(4-chlorobenzyl) sulfide.

Keywords: 4-Chlorobenzyl Chloride, Phase Transfer Catalysis, Ethytriphenyl Phosphonium Bromide, bis(4-chlorobenzyl) sulfide.

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LIST OF SYMBOLS

Q^+X^-	Phase Transfer Catalyst
Q^+	Quaternary Ammonium Cation
MY	Aqueous Phase Reactant
RX	Organic Product
RY	Desired Product
Q_0	Total Initial Catalyst Added
K	Dissociation Equilibrium Constants

LIST OF ABBREVIATIONS

BC	Benzyl Chloride
CBC	4-Chlorobenzyl Chloride
CBM	4-Chlorobenzyl Mercaptan
DBS	Dibenzyl Sulfide
GLC	Gas liquid chromatography
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
TEA	Triethanolamine
DGA	Diglycolamine
DEA	Diethanolamine
PTC	Phase Transfer Catalysis
ETPB	Ethyltriphenylphosphonium Bromide

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

ABSTRACT

This content include the basic understanding of sources of Hydrogen sulphide, important to remove hydrogen sulfide, conventional processes for H_2S removal and recovery used in industries and the objectives of the research work.

Now-a-days preventing the environment from liquid effluents that are polluted by chemical substances is one of the major problems and their treatment is one of the major challenges to the chemical process industry and society. With an increase in the worldwide consciousness to environment protection, chemical engineering is facing various problems with the disposal of environmentally poisonous material in an acceptable manner. Therefore for environmental benefits and for the development of innovative processes, conversion of undesired low valued by-products from chemical industries into some value added products becomes a challenging task for chemical engineers. The present research work is oriented towards a green technology that utilizes the environmentally hazardous chemicals like hydrogen sulfide (H_2S) to synthesize commercially important chemicals to overcome the disposal problems as well as to improve the economy of the process.

1.1. Anthropogenic Sources of Hydrogen Sulfide:

Hydrogen sulfide (H_2S) is a combustible, very noxious, colourless gas with a property of unpleasant eggs smell. Hydrogen sulfide combined with water creates acid sunfuhydric which is the corrosive acid, causing hole sand deterioration and breakable of metal due to hydrogen and it can lead to break the tanks or piping. Hydrogen sulfide arises naturally and from human-made processes. The major anthropogenic source of hydrogen sulfide gas has been petroleum refineries where heavy crude undergoes hydro treatment and hydrodesulphurization during its processing. The natural sources of hydrogen sulfide release from gases like swamplands, volcanoes, sulfur springs, underwater vent and stagnant bodies of water etc. The industrial sources are petroleum refineries during hydrotratment and hydrodesulphurization of crude petroleum and natural gas, furnace plants, food processing plants, and tanneries. H_2S is also associated with manure treatment plants and municipal sumps, swine inhibition and manure-

handling processes, and pulp and paper operations. On the other hand, around 10% of total global discharges of H_2S are from human activity. Hydrogen sulfide is one of the major constituents in the natural sulfur cycle. At very low concentration, human body odour like hydrogen sulfide ranging from 0.0005 to 0.3 parts per million (ppm) but at high concentrations, human may lose their capability to inhale the smell and create very unsafe [Toxological Profile of hydrogen sulfide, 2006].

In processing plants throughout the world are enforced to heavy crude oil containing high quantity of sulfur and nitrogen and also mandatory to hydro-treat the crude oil to bring down the sulfur and nitrogen in level as recommended by environmental agencies. With an increase in the worldwide environmental consciousness, its removal from fluid streams is very desirable due to its toxic and flammable nature. It is also responsible for the harmful problems in subsequent processing steps such as decaying process equipment, deterioration and catalyst deactivation, unwanted product etc (Hamblin et.al, 1973). Hydrogen sulfide is formed after cracking and hydrocracking by the breakdown of sulfur containing molecules present in the oil feedstock at the operating pressure and temperature of chemical plants. Here catalytic cracking involves breakdown of heavy oil to lighter oil for processing into petrol and fine chemicals using a zeolite catalyst and hydrocracking which is a combination of cracking of catalyst and hydrocarbon is used for breaking down heavy gas and vacuum oils. The problem of removing the hydrogen sulfide from the wide variety of feedstock is complicated due to the isolation nature of hydrogen sulfide. Thus in sewerage and municipal waste gases it is accompanied by methane, whereas in refinery gases hydrogen sulfide if found together with methane, hydrogen and higher hydrocarbons and metal containing species which are not completely removed during the process. However reduction of hydrogen sulfide from percentage to ppm level was achieved which include absorption in liquids and oxidation of H_2S using iron, activated carbon or a Claus process. The Claus process is most common technique to eliminate the H_2S from gaseous by-product converted to elemental sulfur. Around 90 to 95 % retrieved sulfur is prepared by the Claus process.

1.2. Requisite for treating H_2S:

Hydrogen sulfide commonly found in natural gas, biogas and LPG. Several indications for the removal of hydrogen sulfide (Occupational and safety health administration) are

1. Hydrogen sulfide is highly detrimental for pipelines. Therefore the treatment of hydrogen sulfide must be essential before transport through pipe. Removal of sulphur from the fluid streams, to be burned as a fuel, may be required to prevent from the environmental contamination due to the formation of sulphur dioxide. To prevent environment pollution, many pipeline specifications limit the amount of H_2S should be less than 0.0088 g/m^3 of gas (Thomas, 1990)
2. Hydrogen Sulfide (H_2S) is a combustible, colourless gas that is very dangerous at low concentrations. It is heavier than air, and can accumulate in low-lying areas. With continuous low level exposure or at high concentration, the victim remains unaware and loses its ability to smell even though it still exists. Low concentrations causes the irritation of eyes, nose, throat and breathing system while high concentration can lead to shock, breathless, rapidly unconsciousness, coma and death. If the level of H_2S gas exceeds 100 ppm, it would nearly be unsafe for life and health. The material safety data sheet (MSDS) of H_2S should be referred for safety purpose**.**
3. Hydrogen sulfide is a poisonous in very low concentrations, highly corrosive gas in presence of air and repeatedly replacement of pipelines, tubing and other apparatus makes the chance of operating natural gas with high levels of H_2S to be breakeven at best. Gas stream must be made completely free from H_2S before use and preferably before transportation**.**
4. Since hydrogen sulfide gas is an inflammable gas, the gas/air mixtures can cause explosion**.** This gas/air mixture may travel to ignition source and flash back**.** If the mixture travels to the ignition source and as a result it gets ignited than the gas from the mixture burns to produce toxic vapours and dangerous gases. The existence of H_2S in the refinery gas streams can hamper the subsequent processes by equipment degradation**,** increase in the process pressure supplies, increase in the gas compressor capacity, deterioration or deactivation of catalyst, unwanted side reactions etc. The various standards of H_2S emissions are shown below Table1

Table1. Standards of H_2S emissions

Industrial Exposure Limit (8h time weighted average)	10 ppm
Public Exposure Limit (for the general population)	0.03-0.006 ppm
Maximum Emissions Limit from sulphur recovery units ➢ 1500 ppmv of sulphur compounds calculated as SO_2 ➢ 1000ppmv of H_2S ➢ 200 pounds per hour of sulphur compounds calculated as SO_2	

1.3. Industrial Process for Removal and Recovery of Hydrogen Sulfide:

Since hydrogen sulfide is highly toxic and corrosive environmental pollutant with an obnoxious smell, therefore it is necessary to remove from the pollution control. The content of H_2S in gas by-product from petroleum refineries, crude petroleum, biogas and natural gas is significantly different and varies from 0.005% to 90% in volume. Due to its toxic and flammable nature as well as the corrosion problems that could occur within industrial plants, its removal from gas streams is very desirable. In industries, several processes have been developed for the removal and recovery of H_2S from various gas streams that bring it concentrations up to acceptable limits for confirmation of strictly environmental conditions. The nature of hydrogen sulfide is acidic, so an alkaline solution is used to remove hydrogen sulfide. Strongly alkaline solution like potassium hydroxide and sodium hydroxide cannot be used to remove hydrogen sulphide. This is due to an irreversible reaction takes place in between weakly acidic hydrogen sulfide and strongly alkaline sodium hydroxide. So far, commercial removal of H_2S has been done by using an alkaline aqueous solution like ammonia and alkanolamine.

1.3.1. Alkanolamines Absorption Process:

Absorption in alkanolamine based process is normally used for removal of acid components. Acid gases like CO_2, H_2S and other sulfuric elements are exist in natural gas and industrial gases to some level. This constituent should remove for economical, operational, eco-friendly reasons. The process contains acidic components that react with an alkanolamine absorption liquid through an exothermic reversible reaction in presence of gas-liquid contactor (Versteeg et al, 2009). One of the major fields of chemical engineering is to remove acid gases in aqueous

alkanoamines solutions such as aqueous solution of mono ethanol amine (MEA), diethanolamine (DEA), di-isopropanol amine (DIPA) and N-methyl diethanolamine (MDEA) and diglycolamine (DGA).

1. Monoethanolamine:

Monoethanolamine ($HOCH_2CH_2NH_2$) is one of the most commercially used alkanolamine for removal of H_2S. The function of the hydroxyl group decreases the vapour pressure and its increases the water solubility of the alkanolamine, and amine group makes an aqueous solution of the compound basic. Therefore, it can neutralize acidic gases such as H_2S. MEA is produced by reacting with ethylene oxide with aqueous ammonia. It is used as feedstock in the production of emulsifiers, detergents, polishes, pharmaceuticals, corrosion inhibitors, chemical intermediates.

2. Triethanolamine:

Conversion of hydrogen sulfide from fluid mixtures containing hydrogen sulfide and other fluids, such a carbon dioxide is done by aqueous solutions containing high purity triethanolamine.it is the first alkanolamine process to become commercially available in industries. Triethanolamine (TEA) was primarily used, but they were replaced by monoethanolamine and diethanolamine solutions because of their maximum reaction rate with acid gases (Gregory and Scharmann, 1937). The disadvantages of TEA are low capacity (due to higher equivalent weight), low reactivity (because of tertiary amine) and its poor stability. Therefore the tertiary amine has been displaced by Diethanolamine (DEA) and monoethanolamine (MEA) due to the lower molecular weights and is proficient to remove complete H_2S.The most important amine that are used for gas purification are Diethanolamine, Monoethanolamine and Methyl-Diethanolamine (MDEA).This alkanolamines have capacity to absorb the total gas acid components.

3. Diisopropanolamine (DIPA):

DIPA is another other secondary alkanolamine that practices in the SCOT Process, ADIP and sulfinol. The reaction rate of DIPA with H_2S is more than CO_2. DIPA is having low steam requirements, and capability to take away sulfur compounds like COS and CS_2. It is low corrosive than other alkanolamines (Haghtalab, 2014). However MDEA is replaced by DIPA due to its resultant removal of H_2S in comparison to CO_2, since MDEA does not take part to form carbamate and presents at the lower rate of reaction with respect to primary and secondary

alkanolamines. Though, MDEA was reported by Kohl and Coworkers at Fluor Daniel (Frazier and Kohl, 1950; Kohl, 1951; Miller and Kohl, 1953) as a selective absorbent for H_2S in the existence of CO_2.

The below mentioned structural formulas of alkanolamines are represented by fig1.1. All alkanolamines is having one hydroxyl group and one amino group. Hydroxyl group decreases vapour pressure and helps in increasing its water solubility. Amine group creates base in the aqueous solution to dissolve acid gases like H_2S.

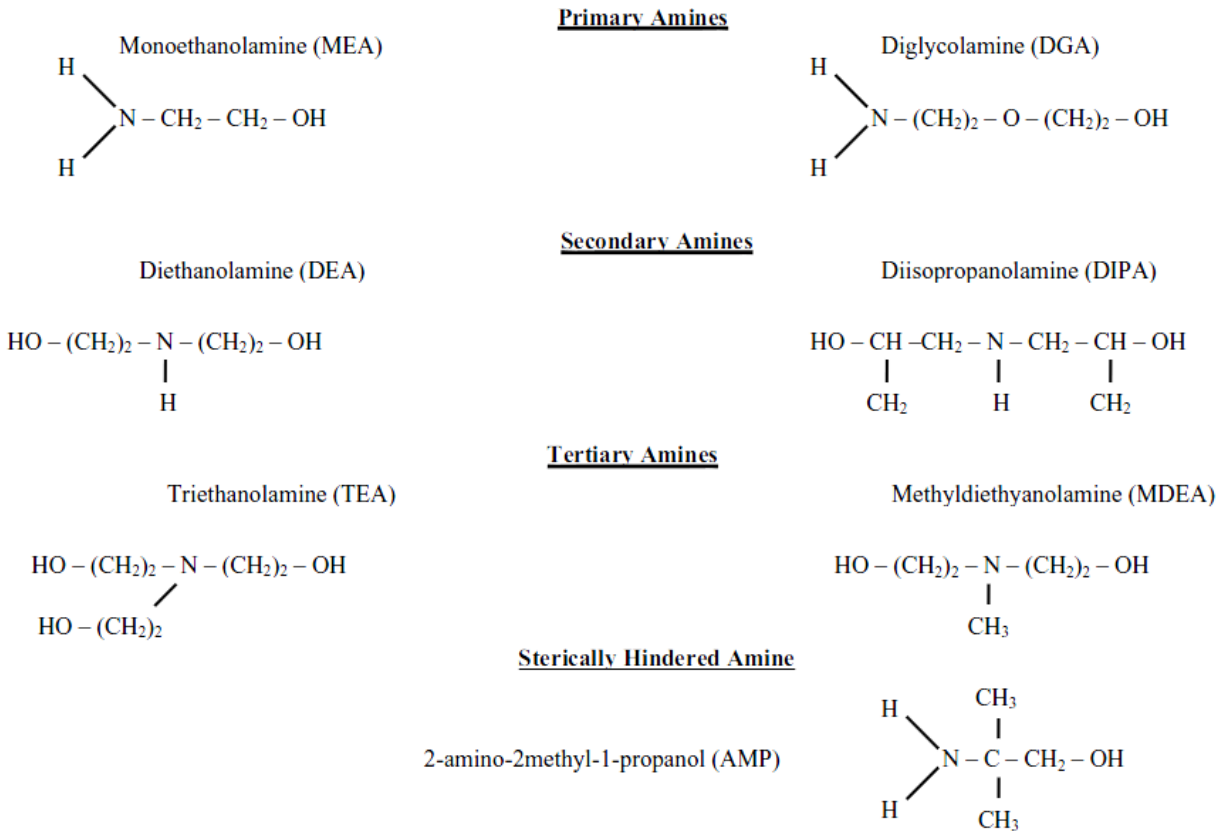


Figure1.1 Structural formula of Commonly Used Alkanolamine

Relationship of various alkanolamine [Warudkar et. al., 2012**]**

1. Monoethanolamine (MEA)

Advantages:

- Primary amine with most reactive reaction
- Low amine circulation rate and easy recovery
- Increases solution aptitude at reasonable concentration due to low molecular weight
- MEA is comparatively strong base with high reaction rate and yielding a low CO2 concentration

Disadvantages

- MEA Concentrations above 30 – 40 wt% and CO_2 above 0.40 moles CO_2 are corrosive
- Heat of reaction with H_2S and CO_2 leads to high energy requirement for stripping
- High volatility causes loss of amine in absorber overhead
- Selective absorption of H_2S from gas stream is impossible
- High heat of reaction

2. Diethanolamine (DEA)

Advantages

- Low volatility because of secondary amine compares to primary amine
- It is suitable for process operation due to its low vapour pressure
- Less acidic than MEA
- Heat of reaction is low
- Due to its low reactivity, the absorption of H_2S for gas stream containing COS and CS_2 can use.

Disadvantages

- High Circulation rate
- Absorption of H_2S is not possible when the gas stream contains CO_2 also.
- DEA go through numerous irreversible reactions with CO_2 to produce corrosive products. Therefore it cannot be the optimal option for handling gases carrying a high $C0_2$ content.

3. Methyldiethanolamine (MDEA))

Advantages

- High selectively of H_2S from gas streams having both H_2S and CO_2
- Energy saving due to the low heat of reaction compared to MEA and DEA.
- Less acidic than MEA and DEA
- Due to low vapour pressure, it used up to 60 wt% in aqueous solution with less evaporation loses.

Disadvantages

- Expensive than MEA and DEA

The basic chemical reactions involves in alkanolamine process are given below using primary amine

Reactions with H_2S:

Sulfide formation: $2RNH_2 + H_2 \rightleftharpoons R(NH_3)_2S$ (1.1)

Hydrosulfide formation: $RNH_2 + H_2S \rightleftharpoons RNH_3SH$ (1.2)

Reactions with CO_2:

Carbonate formation: $2RNH_2 + CO_2 + H_2O \rightleftharpoons R(NH_3)_2CO_3$ (1.3)

Bicarbonate formation: $RNH_2 + CO_2 + H_2O \rightleftharpoons RNH_3CO_3H$ (1.4)

Carbamate formation: $2RNH_2 + CO_2 \rightleftharpoons RNH_3COONH_3R$ (1.5)

Scheme 1.1 Chemical reactions involves in alkanolamine process

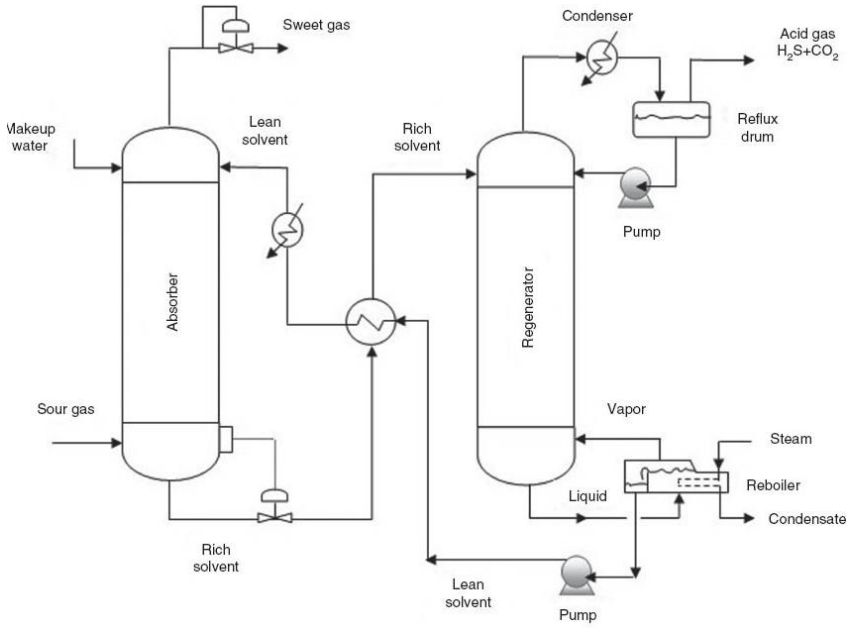


Figure1.2 Schematic diagram of amine-based process for acid gas removal

Process description: The simplified process of acid gas removal with alkanolamines is shown in figure 1.2. The gas feed enters the bottom of the contractor about 70 bar pressure and 30° C temperature. The sour gas flows up in the contactor, counter- currently with the aqueous amine solution. The amine solution is flowing from the top of the contractor where inlet gas temperature was maintained. The contractor operates above ambient temperature due to its exothermic reaction. At the lower portion of the tower, the selective temperature is achieved about 80 °C. The gas which is been treated leaves at the top of the contactor at the temperature of about 38 °C. Around 60 °C temperature, the rich-amine solution leaves from the bottom of the contactor. After that, the pressure of rich amine decreases to 5-7 bar in a flash tank to remove dissolved hydrocarbon. After passed through the heat exchanger, the rich amine goes to the solvent regenerator at the temperature varies at 80 - 100 °C. The vapour streams consist of acid gases and water vapour flows upward to further steps. The regenerator removes the amine and that amine re-enters the top of the contactor to cycle.

1.3.2 Ammonia Based Process:

Removal of H_2S from by-product streams using aqueous ammonia was patented by Hamblin 1973 and Harvey and Makride 1980. In this process, hydrogen sulfide and ammonia present in

gas streams are enters through the H_2S scrubber and NH_3 scrubber in series as shown in the figure. Stripped water is charged to NH_3 scrubber from the top of the column where NH_3 is absorbed. The resultant NH_3 solution enters into the H_2S scrubber. The absorb H_2S containing ammonium sulfide is then charge to the de-acidifier, then decomposes the ammonium sulfide and produces H_2S -rich vapour and NH_3 rich liquor.

The process of ammonia for removal of gas streams like H_2S and CO_2 was proposed by Krupp Wilputte Corporatin, 1988; Davy-still Otto, 1991; and Mitsuibishi Kakoki Kaisha Ltd, 1986, 1986 (Kohl and Nielsen, 1997). The following scheme occurs in ammonia based reactions are:

$$NH_3 + H_2O \rightarrow NH_4OH \quad (1.6)$$

$$NH_3 + H_2O \rightarrow NH_4HS \quad (1.7)$$

$$2NH_3 + H_2O \rightarrow (NH_4)_2OH \quad (1.8)$$

The advantages of using ammonia-based process are:

- An Ammonia-based process is acceptable for gas streams containing both H_2S and NH_3. The elimination of both impurities could be done in a single step in the ammonia-based process while in an alkanolamine-based process. It is done in two steps.
- Ammonia is one of the most mostly produced chemicals in the world. It is a low-cost solvent, does not humiliate in the presence of O_2 and other species in the flue gas, and also less corrosive, in comparison to other amines. The effects of ammonia on environment and health are well considered and found more benevolent than amines. Ammonia has high CO_2 removal efficiency and low regeneration energy.
- Both CO_2 and H_2S Gases come in contact with the aqueous ammonia solution, and then the H_2S is absorbed much more rapidly than the CO_2. Because absorption of CO_2 in weak alkaline NH_3 solution is measured by the liquid film controlled system. The selectivity of absorbed H_2S and CO_2 is feasible in liquid ammonia by changing the concentration of liquid ammonia. The absorption of H_2S gas containing both constituents can be done by using spray column with the combination of short time contact.
- The process is not affected by the existence of carbon disulfide (CS_2), hydrogen cyanide (HCN) and carbonyl sulfide (COS)

The disadvantages of using ammonia-based process are:

All over the world, the acid gas removing technique from a gas stream is not accepted by using ammonical scrubber. A numeral problem connected with its applications (Hamblin, 1973), such as:

- High partial pressure of NH_3 forces the scrubbing step to lead with relatively dilute NH_3 solutions or at relatively high pressures or a distinct water wash step after the NH_3 scrubbing step in order to eliminate NH_3 from the treated gas stream. Moreover, the utilization of dilute scrubbing solutions normally increases considerably the regeneration costs where the regeneration step is performed at a significantly higher temperature than the scrubbing step.
- The regeneration of rich absorbent solution withdrawn from the scrubbing step consists of the use of soluble catalysts, so sulphur products get contaminated in the bearing of the catalyst.

1.4. Method of Oxidation of H_2S:

1.4.1 Claus Process:

Hydrogen sulfide is highly toxic, corrosive gas and it is also deactivated industrial catalysts. Due to this obnoxious substance, it is needed to be converted to nontoxic and useful elemental sulfur before it uses for the further application. Therefore the process of choice is Claus Sulfur Recovery process. Around 90-95 % of recovered sulfur is produced by the Claus process. In 1883, Chemist Carl Friedrich Claus first patented the Claus process which has the mostly use process for sulfur recovery in the industry. The by-product gas streams mainly originate from physical and chemical gas treatment units (Selexol, Rectisol, Purisol and amine scrubbers) in various refineries, natural gas processing plants and gasification or synthesis gas plants. These by-product gases may also contain hydrogen cyanide, hydrocarbons, sulfur dioxide or ammonia.

Description of the Claus process:

Firstly, H_2S is separated from the gas stream by using amine extraction. After the extraction process, it is introduced to the Claus process. There are two process steps in Claus technology for converting to elemental sulfur.

Thermal step:

In thermal step, the H_2S-rich gas reacts in a sub-stoichiometric combustion in a furnace at high temperatures above 850^0C where elemental sulfur precipitates in a downstream process gas cooler. Claus gases (acid gas) with no further flammable contents apart from H_2S are burned. The thermal step which is exothermic free-flame oxidation reaction produces sulfur dioxide. The following reaction is occurring in thermal step.

$$2H_2S + 2O_2 \rightarrow SO_2 + 2H_2O + S \qquad (1.9)$$

This reaction shows that total 1/3 of hydrogen sulfide is transformed to SO_2, make sure with a stoichiometric reaction for the Claus reaction in the second catalytic step. Generally 60 to 70% of the total amount of elemental sulfur produced in the thermal process.

Catalytic step:

The remaining H_2S from the Claus furnace is contact with the SO_2 at lower temperatures (about 200-350 deg C) over a catalyst like activated aluminum (III) or titanium (IV) oxide and it's converted to produce sulfur.

$$2H_2S + SO_2 \leftrightarrow \frac{3}{8}S_8 + 2H_2O \qquad (1.10)$$

In catalytic step, mainly S_8 is produced and it is an exothermic reaction. On the contrary in thermal step, S_2 is the major product and the reaction is endothermic nature. About 70% of H_2S and SO_2 will react in this reaction. The recovery of sulfur consists of three process steps. There are heating, catalytic reaction and cooling condensation. Here the first route step in the catalytic step is the gas heating process.

There are some demerits of using Claus process for recovery of hydrogen sulfur:(Plummer,1994; Plummer and Beazley, 1986; Plummer and Zimmerman, 1986)

1. The valuable product like hydrogen is not recovered but converted to water.

2. The conversion of elemental sulfur is not 100% due to tail gases cleanup may exceed the monitory benefit of the recovered sulfur.

3. Process controls at high temperature.

4. Requires rigorous process control to maintain the ratio of oxygen to H_2S in the feed.

5. If CO_2 is present in high concentrations, it requires expensive pre-treatment of the feed gas. Therefore CO_2 must be removed from the byproduct gas by pretreatment before oxidizing the H_2S to maintain the efficiency of the oxidation process.

6. The sour gas from the Claus process is released to the atmosphere is generally too high to meet stringent environmental regulations. To overcome the principles, it is necessary to add more Claus stages and/or employ a separate gas cleanup process at great expense.

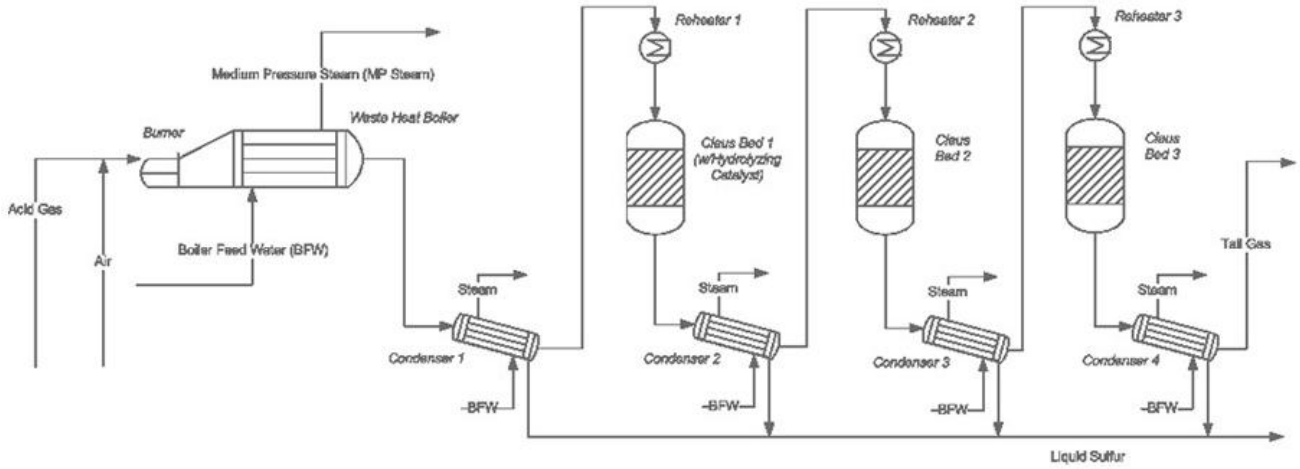


Figure1.3 Flow diagram of sulphur recovery unit (Claus process)

1.4.2 Crystasulf Process:

The CrystaSulf is a new nonaqueous sulfur removal process from gashouse H_2S and converts it into nontoxic solid sulfur by-product. First publication based on CrystaSulf was reported in 2001 and to develop specifically to treat high-pressure natural gas. The features of the selection of CrystaSulf are low circulation rate with high-pressure absorber, low pumping cost. In this process, about 1/3 of the total H_2S in the natural gas is first oxidized to SO_2 at low temperatures over a heterogeneous catalyst (Lundeen at el.2012). Low temperature oxidation is done so that the H_2S can be oxidized in the presence of methane and other hydrocarbons without oxidation of the hydrocarbons.

First H_2S is separated from the sour gas in a conventional tray absorber then reacts with dissolved sulfur dioxide to produce high solubility elemental sulfur. From the absorber, the rich sulfur solution is then passes through the flash tank where the solution flows to a crystallizer and form solid elemental sulfur crystals at lower temperature. The lean solution overflows from the crystallizer to a tank, where a heater increases the solution temperature back to the circulating temperature and realized that all elemental sulfur is dissolved within the solution. The following chemical reaction in this process is

$$2H_2S + SO_2 \leftrightarrow 3S + 2H_2O \qquad (1.11)$$

1.4.3 Wet -Oxidation Lo-Cat Process:

Wet-oxidation LO-CAT process by US Filter/Merichem is an attractive method to remove H_2S that utilizes chelated iron catalyst. The Chelated iron catalyst is used to convert hydrogen sulfide to nontoxic elemental sulphur. The iron catalyst is introduced into the solution by using organic chelating agents that wrap around the iron in a claw, preventing precipitation of either iron sulphide (FeS) or iron hydroxide ($Fe(OH)_3$). The environmentally safe iron catalyst oxidizes the sulphide ions to elemental sulphur in which the iron is reduced from ferric state to the ferrous state. The iron which is being reduced is then regenerated back from the absorber to the oxidizer and reacting with oxygen (air).

1.5 Methodology of Present Process

The present work is based on the idea of using waste hydrogen sulfide compound which is produced as by-product during hydrotreatment of heavy, sour crude oil etc. The work involves process development for the production of high commercially important aromatic thioethers using H_2S–rich commercially important alkanolamine like Methyldiethanolamine (MDEA). It has very high commercial important due to the replacement of the expensive Claus process which gives elemental sulphur as the only product. The work is deals with the synthesis of valuable chemicals like bis(4-cholorobenzyl) sulfide and 4-chlorobenzyl mercaptan from H_2S rich gas streams acquired from various industries that is usually considered as a waste. Therefore to prevent from environmental waste, various amines like Methyldiethanolamine (MDEA) is used to absorbed the hydrogen sulfide. The present research work aims to achieve the following

- Absorption of hydrogen sulfide in alkanolamine like methyldiethanolamine(MDEA) to get desired H_2S–rich amine solution which will be used as sulfiding agent for the selected aromatic halides.
- Synthesis of value added chemicals like bis(4-cholorobenzyl) sulfide and 4-chlorobenzyl mercaptan from 4-chlorobenzyl Chloride and H_2S rich MDEA using Ethyltriphenyl phosphonium bromide (ETPB) as a PT catalyst under L-L PTC condition.
- Kinetic studies and experimental optimization to know the effect of different process variables like stirring speed, concentrations of reactant and catalyst, sulfide and MDEA concentrations in aqueous phase, temperature and different catalyst concentration for increasing conversion and selectivity of desired product. Also find out the optimum process condition to maximize the yield of desired product.
- Development of mechanism of the reaction for finding out the pathway of the synthesis process.
- Estimate the reaction parameters like an order of reaction, activation energy, enhancement factor etc.

1.6 Phase Transfer Catalysis:

Phase transfer catalysis (PTC), a broadly used technique for directing synthesis reactions between two immiscible phases in a heterogeneous reaction system. Phase transfer catalysis is mainly used in industry, particularly in organic synthesis of organics such as pharmaceuticals, dyes, chemicals etc. In comparison with dipolar solvents that are a very expensive and difficult to recover, PTC has some advantages in terms of reaction conditions and economy. The basic premise of Phase transfer catalysis simply PTC of the two insoluble phases is the selected phase transfer agent that, used in catalytic quantities, can bring one of the reactants into normal phase of the other reactant that gives high reaction rates (Starks et. al. 1978). In this phenomenon, one phase acts as a reacting anions and other phase, which is the organic phase, comprises the organic reactants and catalysts generating lipophilic nature. The reacting anions enter the organic phase in ion pairs with lipophilic cations via phase transfer catalyst. Through mutually immiscible phases does not react the reaction unless the catalyst Q^+X^- is present. Hence the catalyst facilities the reacting anions into the organic phase in the form of lipophilic ion-pairs due to ion-exchange equilibrium (1.12). On the other hand, anions react in organic phase as in

nucleophilic substitution reaction as shown in equation 1.13. Here alkyl halides go through nucleophilic substitution reaction. Other reactions such as addition, reduction, oxidation, eliminations, hydrolysis etc have been catalyzed by anion transfer using this approach.

$$Na^+Y^-_{aq} + Q^+X^-_{org} \rightarrow Na^+X^-_{aq} + Q^+Y^-_{org} \quad (1.12)$$

$$Q^+Y^-_{org} + R-X \rightarrow R-Y + Q^+X^-_{org} \quad (1.13)$$

The advantages of phase transfer catalysis are:

- Feasibility in the presence of water and avoidance of run-away condition
- Minimization of industrial wastes
- Mild reaction condition
- Elimination of inconvenient, hazardous and costly reactants
- Increases the reaction rates and selectivity of the active species
- Low energy consumption
- Mild reaction conditions, which increase process reliability and flexibility

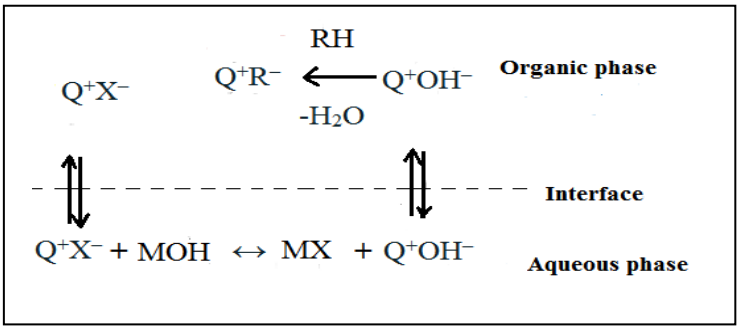
1.6.1 Mechanism

The mechanism of PTC reaction was first suggested in 1971 by Starks. Mechanistic aspects of phase-transfer catalysis remain ambiguous, mainly due to the biphasic systems and the many complex parameters that must be analyzed. Two proposed mechanisms are given below.

1.6.1.1 Starks Extraction Mechanism

According to Starks' mechanism, phase transfer catalyst dissolved in the aqueous phase that creates the anion exchange reaction with the anion of the reactant. Due to the lipophilic nature of the catalyst, transmission of ion pair is made with the liquid-liquid interface into the organic phase. The organic phase anion is quite nucleophilic undergoes a nucleophilic substitution reaction with organic reagent and form the desired product. Subsequently catalyst recycles back to the aqueous phase and cycle continues. For example, the quaternary salt of catalyst (Q^+X^-) reacts with inorganic base (MOH) in the aqueous phase and removes hydroxide from the aqueous phase. Due to lipopilicity of quaternary hydroxide (Q^+OH^-), it can move from the

aqueous to organic phase and then remove hydrogen from the acidic organic compound to give the reactive intermediate Q^+R^-.



(X^- = tetra alkyl ammonium or phosphonium salts, MOH = inorganic base)

Figure1.4 Schematic diagram showing Starks extraction mechanism

1.6.1.2 Makosza Interfacial Mechanism

Makosza in 1969 formulated the first mechanistic hypothesis on PTC. The interfacial mechanism pathway is an initial creation of metal carbon ion at the interface in the absence of phase transfer catalyst. Here metal salt having organophilicity nature can transfer from aqueous to organic phase through the interface. The main reaction occurs in organic phase only. PTC is not involved in anion exchange step. The mechanism is more applicable for highly lipophilic PTC and reluctant to enter aqueous phase.

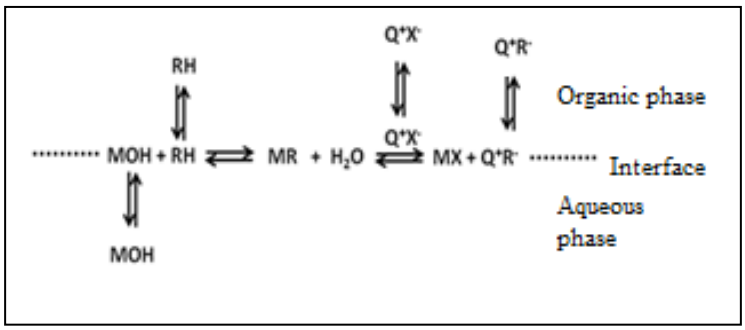


Figure1.5 Schematic diagram showing Makosza interfacial mechanism

1.6.2 Classification of PTC

There are two main types of PTC reaction, Soluble and Insoluble. Based on actual aqueous phase and organic phase present in the reaction system, the soluble PTC is further classified into liquid-liquid (L-LPTC), solid-liquid PTC (S-LPTC) and gas-liquid (G-LPTC). For the soluble catalyst, recovery and separation of catalyst becomes complex. Therefore, there is another form of PTC called third liquid phase where catalyst rich part created third phase in between organics and aqueous phase. The classifications of these catalysts are given below.

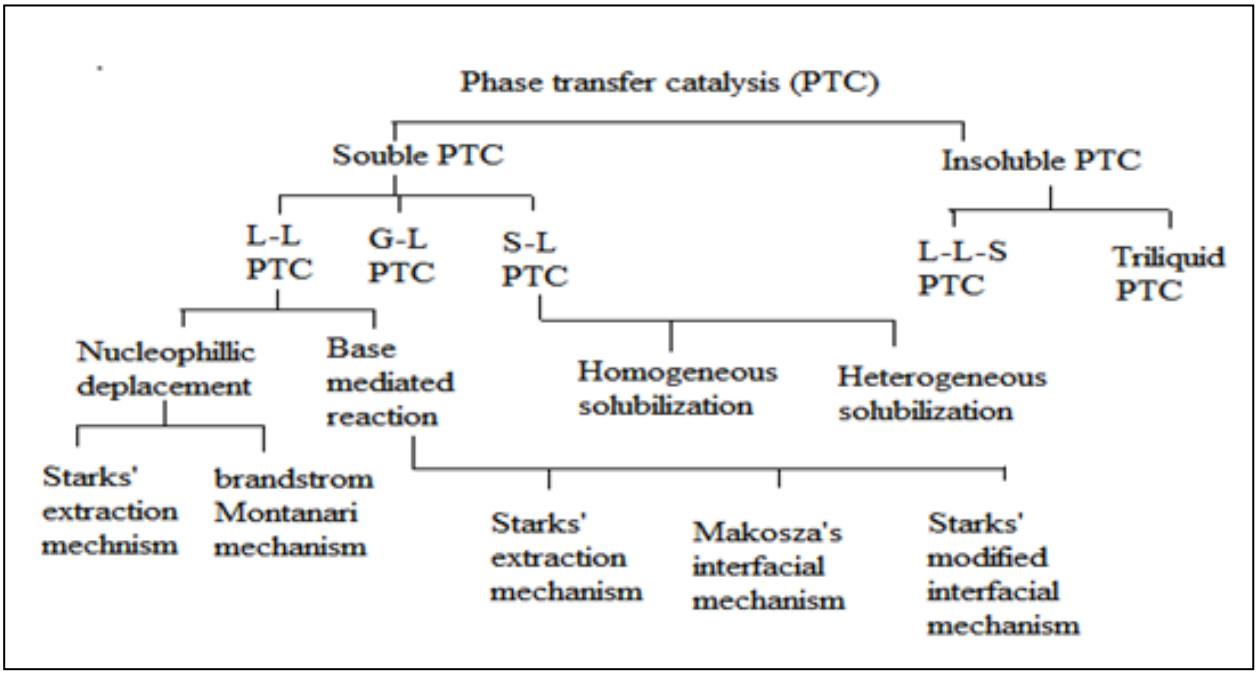


Figure 1.6: Classifications of PTC

1.6.2.1 Solid-Liquid PTC:

Most of the industrial processes undergo the disadvantages by using L-L system such as unwanted side reaction, non-recovery and non-reuse of the catalyst. To eliminate the problems, the solid form of nucleophile is engaged which is suspended in the organic phase, known as solid-liquid (S-L) PTC. Therefore, more yield and selectivity can be obtained by using S-LPTC than L-LPTC. Solid-liquid PTC is used for accompanying a variety of organic transformations. In solid phase, the reactant contains an anionic reagent, where reactant located in adjacent liquid organic phase. Therefore the transport of a reactant anion from the solid phase to the organic phase is by the phase-transfer cation. The next step involves the reaction of the transferred anion

with the reactant situated in the organic phase. In this process quaternary active catalyst Q+X- which is in solid surface undergoes ion exchange with solid nucleophilic salt adjacent the solid surface and formed Q+Y-, followed by the reaction of Q+Y- with organic subtract RX. Here organic reaction takes place in the liquid phase. Based on location and mechanism of ion exchange reaction and solubility of the solid in organic phase, S-LPTC is further classified to homogeneous and heterogeneous solubilisation (Miville and Goddard, 1988; Naik and Doraiswamy, 1997). Homogeneous solubilisation is that the nucleophilic salt (KY) has some limited solubility in the organic phase and involves the dissolution of the inorganic salt in the organic phase. PTC cannot approach directly with solid surface but exchanges the anion with dissolved MY in the organic phase and react with Y- to form Q+Y-. The heterogeneous solubilisation PTC can transfer the nucleophilic anion from the solid surface of the solid crystal lattice to the organic phase. The PTC reacts with solid at the interface and combines with anion Y- and ferries back to organic phase in the form of Q+Y- followed by the organic reaction between Q+Y- and RX in the liquid phase as shown in Fig. 1.7

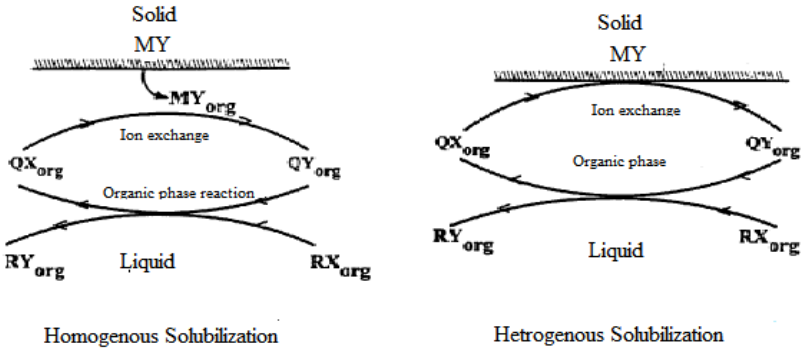


Figure1.6 Solid-liquid PT catalyst

1.6.2.2 Gas-Liquid PTC:

From a sensible purpose of read, GL-PTC is also connected with the final category of supported liquid-phase catalyst (SL-PC) (Rony et.al, 1968) processes, during which a gaseous chemical agent flows through a solid red bearing a liquid catalyst. In gas-liquid PTC, reactions are carried out in a thermostatized glass column which is contain solid bed of solid salt of the nucleophile or of a base able to generate and to absorbed on solid. The organic subtract are charged into the

column where pressure and temperature maintain both reagents and products in the gas phase. At the outlet column, the mixture was continuously collected by condensation. The gaseous phase contained organic substrate, is disregarded a bed of solid inorganic chemical agent coated with phase transfer catalyst in liquid-liquid kind shown in Fig. 1.8 below. The gaseous reactant RX diffuses through liquid PT catalyst for organic synthesis. Though, it's a tri-phase system, historically referred as a GLPTC. PT catalyst will simply recover because it's directly loaded on inorganic solid bed and enhance property is obtained to get an organic chemical in gaseous form; method is administered at an extreme temperature. Extreme temperature could also be typically to blame for thermal decomposition and fractional volatilization of PT catalyst. So the selected catalyst should have sufficient thermal stability (Tundo . et al., 1989).

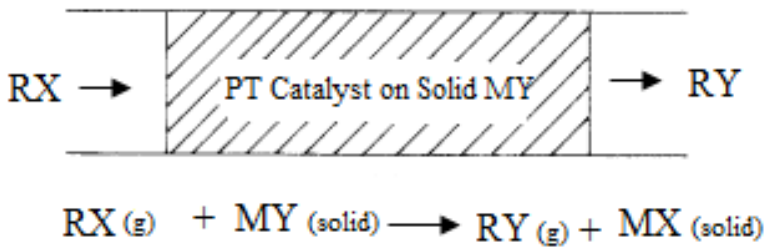


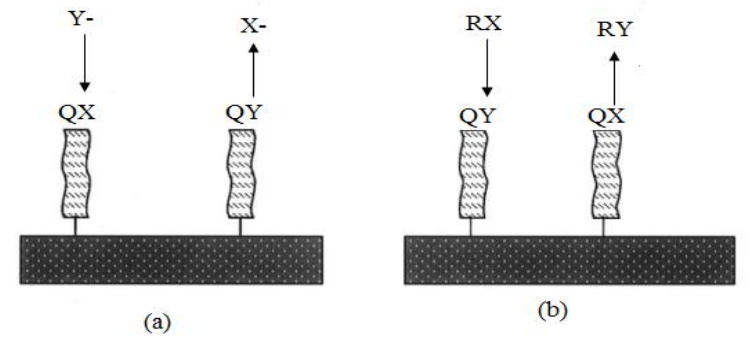
Figure1.7 Mechanism of G-L PTC

1.6.2.3 Insoluble Phase Transfer Catalysis:

The problem facing in phase transfer catalysis (PTC) by soluble PTC is that the removal of catalyst from reaction mixture cannot possible. This affects the cost and also affects product purity, by-product disposal and environmental concerns. Some of the widely used processes like distillation, extraction and absorption is use to separate of catalyst and product from reaction mixture. But in distillation column, it is becomes an energy consuming process if the relative volatility between product, catalyst and solvent are very low. Other solvent is required in case of extraction and absorption which again has to be extracted off (Yadav and Lande, 2005; Yadav and Desai; 2005). Consequently, catalyst is considered as a waste due to its small (Jin et al., 2003). For such purpose, insoluble catalysts are used due to its easy separation and potential for recycle. Commercially available ion exchange resin is used as an insoluble PTC.

1.6.2.4 Liquid-Liquid-Solid Phase Transfer Catalyst:

L-L-S PTC which is commonly named as triphase catalysis (TPC) involves solid supported catalyst such as polymer resin or inorganic solid with two immiscible liquid phase reagents (G.D Yadav et.al 2000). Conventional soluble PTC has disadvantages that chemical techniques such as distillation or extraction are used to separate the catalyst from product is quit complicated and significantly affect the cost and purity of the product. Therefore triphase catalyst is a method to overcome the problem by immobilizing the PT catalyst on a solid support. Compare to conventional PTC, TPC can be used as easy recover, recycling of catalyst etc. Here simple filtration step is used to separate the catalyst and recycle for further use. In triphase organic phase act as a substrate or dispersed phase and aqueous phase act as a reagent or continuous phase. Triphase which is typical heterogeneous catalyst system consists of an ion exchange step in aqueous phase followed by the organic phase reaction. The catalyst movement is restricted in TPC system. An organic and aqueous phase must be travelled to catalyst cation (Justin A.B. Satrio et al., 2000). Fig. 1.9 shows systematic representation of Triphase system. The disadvantages of TPC are higher initial cost and lower catalytic activity due to diffusion limitations



X- and Y- = inorganic nulceophillic and leaving anion in the aqueous phase

RX and RY=organic substrate and organic product

Figure1.8 L-L-S phase transfer catalyst (a) Aqueous Phase Reaction (b) Organic Phase

1.6.2.5 Liquid-Liquid-Liquid PTC:

If the solubility of phase transfer catalyst is limited in both aqueous phase and organic phase, then third liquid phase is introduced in the middle. In L-L-L PTC, main reactions take place in the third liquid phase where both the organic phase and aqueous phase ions transfer to third phase (Yadav et. al. 2010).The third phase reaction becomes the main reaction phase to enhance the reaction rate and increase the selectivity of the desired product. As economy and environmental benefits are concern, the catalyst rich third phase can be recover and recycle as well as aqueous phase can also be reused a few times. Third phase of liquid happens when concentration of catalyst reaches a critical value. If catalyst concentration is below the critical point then the third phase will disappear and converts itself into bi-liquid phase PTC system (Yadav et.al 2008). The disadvantages of third phase are requirement of high quantity of catalyst and loss of catalyst activity due to the loss of catalyst concentration in both aqueous and organic phase at each run of the reaction mixture. The below reaction mechanism implies the third liquid phase PTC.

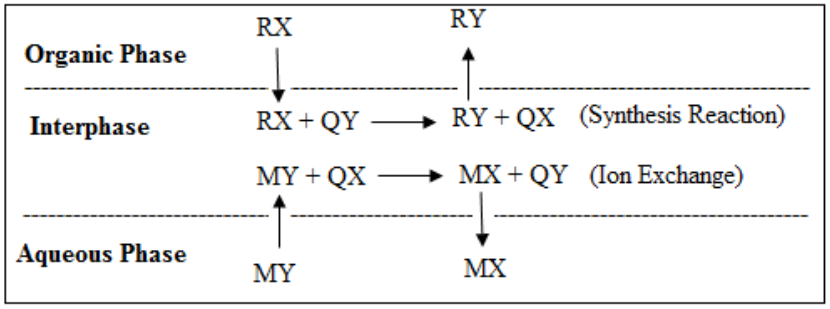


Figure1.9 Third phase PTC

1.6.3 Types of Phase Transfer Catalyst

A variety of phase transfer catalysts exist, such as onium salts (quaternary ammonium and phosphonium salts), macrocycyclic polyethers (crown ethers), aza-macrobicylcle ethers (cryptands), open chain polyethers (Polyethylene glycols), etc. Among these, the quaternary ammonium salts are the most widely used in the industry. PEG'S are the cheapest and crown ethers, and cryptands are the most expensive of the commonly used PT catalysts. Since PEG'S,

crown ethers, ionic and cryptands are more stable at higher temperatures, these catalysts can be used up to temperatures of 150-200ºC. It is important to note that many applications of PTC require temperatures of 50-120ºC and quaternary onium salts are very active, stable, and widely appropriate under these conditions. Crown ether, cryptands, and PEG'S also have higher stability to basic conditions than quaternary onium salts. Moreover, the separation and recovery of catalyst are also important challenge. Solid phase transfer catalyst,commonly recognised as reusable reagents have attracted growing attentions, by reason of their specific advantages, such easily recovering and reusing of the catalyst. Table 2 summarizes the properties common PT catalyst.

Table 2: Properties of frequently used phase transfer catalyst

(Naik and Doraiswamy. 1998)

PT Catalyst	Cost	Activity and Stability	Applications and Recovery of catalyst
Ammonium salts	Low cost	Moderately active and stable upto 100^0C Decomposed by Hofmann elimination reaction under basic conditions	Commonly used. Relatively difficult to recover.
Phosphonium salts	Expensive than ammonium salts	Thermally stable than ammonium salts. Decompose under some basic conditions.	Large application. Difficult to recover.
Crown ethers	Expensive	Highly active and stable at temperature upto 150-200^0C.	Hardly used. Difficult to recover Poses environmental issues due to their toxicity.
Cryptands	Expensive	Highly active and stable at high temperature but unstable in presence of strong acid.	Often used due to high cost and high activity. Difficult to recover due to toxic nature.
Polyethylene Glycol	Cheapest	Low activity. More stable than quaternary ammonium salts.	Often used. Large quantity of catalyst does not affect the reaction system. Recovery is quite easy

CHAPTER 2

LITERATURE REVIEW

2. LITERARURE REVIEW

2.1.1 Use of Aqueous Alkanolamine for Removal of H_2S:

Now a days, aqueous alkanolamines are broadly used in productions for the removal of waste sulfur compound i.e. Hydrogen Sulfide (H_2S) which is unutilized by-product of industries like petroleum and natural gas processing industries as discussed in chapter 1. Many researchers has investigated the study on pure H_2S containing both acid gases H_2S and CO_2 based on the equilibrium solubility acid (Lee et al., 1976; Lawson and Garst, 1976; Sidi-boumedine et al., 2004). Research has also been carried out to utilize H_2S-Rich alkanolamine to produce value added chemicals like dibenzyl sulfide using nitrogen containing insoluble Phase transfer catalyst (PTC) (Maity et. al. 2007; Sen et al. 2011)

Ganz et al.1995 examined the degree and rate of adsorption of hydrogen sulphide by aqueous solutions of ammonia. H_2S adsorption was completely achieved with use of mechanical absorbers in presence of high turbulence.

The recovery and the removal of H_2S from by-product streams using ammonium hydroxide are patented by Kohl and Nielsen in 1997. Here the ammonium hydroxide and absorbed H_2S were used to produce ammonium hydrosulfide. Further oxidation of ammonium hydroxide with an air stream to get a waste stream containing ammonium polysulfide and to recover elemental sulphur, polysulfide was treated. Litvinenko et al.1965 developed a pilot plant to remove H_2S from coke oven gas and combine with NH_4OH to form $(NH_4)_2S$. Asai et al. 1989 considered the rates of simultaneous absorption of H_2S and NH_3 into water in an agitated vessel with a plane interface and simultaneous solubility of H_2S and NH_3 in water was showed by Rumpf et al in 1999.

The development of two –film model with mass and heat transfer during the rate based model of CO_2 chemical absorption using alkanolamine solutions was studied by Xixi Liu 2014.

2.1.2 Preparation of Chlorobenzyl Mercaptan:

Limited information is published based on proposed method for the production of mercaptans using H_2S (Maity et al, Sen et al. 2006). However information related to the present topic is given below.

Benzyl mercaptan is valuable as a raw material for the production of various biologically active materials as well as production of herbicides in the thiocarbamate family (Labat, 1989). Purity of benzyl mercaptan is excellent for further use. It is used to synthesize antihypertensive and diuretic drugs like benzthiazide (R.L Jagadish et al, 2002). It is also used to synthesis esprocarb, tiocarbazil, prosulfocarb etc (Maity et al, 2003**).** The synthesis of benzyl mercaptan from hydrogen sulfide with benzyl alcohol using catalyst is not economically feasible due to the high cost of benzyl alcohol and its undesirable characteristics during catalysis (deactivation of catalysts and rapid loss of selectivity (Yves Labat, 1991). His patent was based on the synthetic route of benzyl mercaptan by reacting with benzyl chloride and ammonium sulfhydrate.

James Heather invented a method of preparation of benzyl mercaptan where benzyl halide reacts with hydrogen sulphide atmosphere at a temperature about 50^0C and conversion has achieved approximately 90% of the starting material. The present invention is related to a method for the preparation of benzyl mercaptan, an intermediate compound used in the preparation of S-benzyl thiolcarbamates, compounds which are known as herbicides.

A novel method of preparing mercaptans was first invented by John L. Speier in 1978. His study was involved with a mixture of H_2S react with an organic chloride or bromide and an amine at certain temperature under autogenous pressure in presence of polar solvent.

2.1.3 Preparation of Bis(4-Chlorobenzyl) Sulfide

Sodium sulfide is well recognized for the preparation of diaryl sulfides. The halides like benzyl chloride and p-chlorobenzyl chloride react with sulfide ions to give desired product diaryl sulfide was studied by Narayan et al.1990 existing of phase transfer catalyst TBAB. Diaryl sulfide has various applications such as additives for extreme pressure lubricants, motor oils antiwear additives, as stabilizers for photographic emulsions, in numerous anticorrosive formulations. He compared the various systems L-L and S-L in presence of catalyst and absence of catalyst. It had been seen from the results that benzyl chloride was 2 times more reactive than p-chlorobenzyl chloride in S-L system whereas P-chlorobenzyl chloride was 2 times faster reacting than benzyl chloride in L-L system in presence of catalyst.

Kim and Noh (1975**)** in presence of phase transfer catalyst Aliquat 336 with aqueous sodium sulphide and p-nitrochlorobenzene to give selective bis(p-nitrophenyl)sulphide.

Evans (1984) has outlined the synthesis of diaryl sulfides by the phase-transfer-catalyzed interaction of sodium sulfide with liquid aryl halides. Within the case of the synthesis of water-sensitive diaryl sulphides, the technique was vital. The yields of diaryl sulfides are defined to be greater than 50% when activating groups such as nitro, cyano, phthalimido and anhydrido are present in the aromatic compound. In the absence of these activating groups, the conversion is less than 2%. The work has attributed to the greater activity of aryl halides and additionally to the result in solvent polarity within the presence of the activating groups.

The originalities of phase transfer catalysed reaction etherification of phenol with benzyl chloride in a triphase L-L-L mode have deliberated by Yadav (2007)**.** To enhance the selectivity and to waste minimization strategy, L-L PTC converted to L-L-L to recover and utilize the catalyst. Sodium chloride and catalyst concentration were a main factor for forming the third phase and distribution of catalyst.

Naheed Sidiq (2014) investigated the conversion of halides to disulfides using sulphur-transfer chemical agent like ammonium tetrathiomolybate (BTATM). He justified a nucleophilic substitution: carbon-metal-carbon reaction mechanism. As per mechanism is concern, he suggested that benzyl halides gave more monosulfide product than alkyl halides and higher percentage of RSR observed in case of benzyl chloride compared with benzyl bromide, attributed to fact that bromide was a better leaving group.

Synthesis of dibenzyl sulphide was also well documented using PTC technique. Aromatic thoiether was produced by Sen et al**.** in 2006 from BC and ammonium sulfide in L-LPTC using PT catalyst. The observed work shows the high DBS selectivity with high catalyst, ammonia and BC concentration at 50^0C. Then Sen et al**.** in 2011 synthesize DBS from H_2S rich MEA and BC and witnessed that MEA is good absorbent than ammonia and high concentration of MEA was required for high DBS selectivity.

2.1.4 Liquid-Liquid Phase Transfer Catalyst:

The advantage of using Liquid-liquid PTC reactions are conducted under mild conditions, using less expensive solvent at much faster reaction rates and enhance selectivity of the desired product and problems of using L-L from environmental characteristics is that the catalyst distributed both

the phase so normally it is not recovered or reused. Hence it is treated as waste due to small quantity and do not contribute much to the high-priced product.

To overcome the demerits of L-L system, Ganapati D.Yadav, Sharad V Lande (2007) modified L-L PTC and convert to Tri-liquid (L-L-L) system to intensify the rates and to recover and reuse the catalyst by using immobilizing the catalyst on porous solid support.

Ganapati D.Yadav and Smruti P.Tekale (2010) studied the selectivity of o alkylation of 2 naphthol using phosphonium based ionic liquid under the different mode of phase transfer catalysis such as trihexyl-(tetradecyl)-phosphoniumchloride (THTDPC) ,Tri-hexyl (tetradecyl) phosphonium bromide (THTDP), trihexyl(tetradecyl)phosphonium decanat (THTDPD) and tri-hexyl (tetradecyl) phoasphonium-hexafluorophosphate (THTDPH). According to work, THTDPB as a catalyst has high reactivity which is dependent on the anion attached to phosphonium cation than others. In this studied, 100% selectivity was found and also studied the reusability of ionic liquid.

Liquid- liquid phase system is used to synthesize benzyl acetate by reacting with benzyl chloride and sodium acetate was investigated by Sang-Wook Park in 2003. His research work was to analyse the kinetic of the reaction of benzyl chloride and sodium acetate are simple ion exchange across interface and anion exchange in the aqueous phase.

Reduction of nitrotoluene using an aqueous sulphide as reducing agent was carried out in organic solvent under L-L PTC in presence TBAB .Selectivity of product was found to be 100% (Maity S K , Pradhan N.C. Patwardhan A.V 2006)

Dehmlow et al,1993; Starks et al,1994 generalized an approach based on the experimental data that the liquid-liquid phase transfer catalyzed reaction uses a pseudo-first order reaction. This model could describe the complicated nature of L-L reaction because catalyst dissolved in both the organic and aqueous phase.

Yang h, Lin c.(2003) studied the reaction between benzyl bromide and sodium benzoate in L -L system using aliquate- 336 phase transfer catalyst using chlorobenzene as a solvent . 98% product yield was obtained.

Kinetics of chemo- selective reduction of citronellal to citronellol by sodium borohydride was studied by Yadav G. D, Lande Sharad V using tetra-butylammonium bromide (TBAB), tetra-propylammonium-bromide (TPAB), Tetra-ethylammonium-bromide (TEAB) and tetra-butylammonium hydrogen sulfate phase transfer catalyst. Here TBAB was found as best catalyst among those catalysts.

2.1.5 Ethyl Tri Phenyl Phosphonium Bromide (ETPB) as Phase Transfer Catalyst:

Phosphonium salts which are derivative of phosphine and phosphorous are employed primarily as phase transfer catalyst. The applications of phosphonium catalyst are lubricatns, electrolytes, paramagnetic fluids, entrainers, extractants for sulphur containing compounds etc. The phosphate organic molecular crystals are very enthusiastic for different kind of photo induced effects due to large anisotropy in the chemical bonds intra-the phosphate groups and inter-molecular weaker Chemical bonds (Krishnakumar et al. 2009). Ethyltriphenylphosphoium bromide (ETPB) is white to off-white crystal-like powder and its chemical formula $C_2H_5P(C_6H_5)_3$. It is used as phase transfer catalyst in the production of epoxy resins and powder coatings and as a pharmaceutical intermediate. Hence the present investigation deals with ETPB compound as a phase transfer catalyst. The molecular structure of Ethyltriphenylphosphonium bromide (ETPB) is shown below.

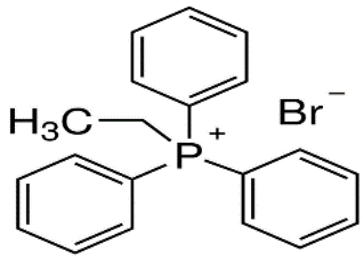


Figure 2.1: Molecular structure of ETPB

Various catalysts having different cationic and anionic structure such as TBAB, TBAHS, TPAB, TEAB and ETPB were employed under S-L PTC to synthesized etherification of vanillin through benzyl chloride (Yadav et.al. 2006). The order of activity was establish to be as follows TBAB>TBHS>TEAB>ETPB.

Based on experiment, higher molecular weight better is the partition in the organic phase. Br- is better anion than hydrogen sulphate. At low temperature, quaternary ammonium salts are better than phosphonium. The best catalyst among other catalyst used is found to be TBAB.
The advantages of phosphonium ionic liquids over ammonia salt are

- Improved chemical stability under different conditions; more thermally stable than ammonium and imidazolium salts.
- Both ammonia and phosphonium based catalyst can decompose at elevated temperature, phosphonium salts are generally more stable even at above 300^0C.Whereas ammonia salts decompose at approximately lower temperature.
- Phosphonium salts depict higher electronic polarizabilities than their ammonia.

In the view of these publications, the conversion of desirable product has been slow so far. Phosphonium based containing PTC has been tried in many conversions with considerable better success in terms of conversion (Yadav et. al. 2003). In this work phosphonium based phase transfer catalyst like Ethyltriphenyl phosphonium bromide are being tried out to convert 4-chlorobenzyl chloride into respective thioether.

Few researchers have studied the synthesis of benzyl chloride and benzyl mercaptan in presence of PTC catalyst. No one has studied the diaryl sulfide like bis(4-chlorobenzyl) sulfide using organic halide and H_2S-rich MDEA aqueous solution. There is no publication based on the preparation of Bis(4-chlorobenzyl) sulfide in presence of ETPB catalyst .

CHAPTER 3

EXPEIMENTAL

3. EXPERIMENTAL

3.1 Chemicals:

Preparation of H_2S rich MDEA

- Sulfuric acid from Merck Pvt. Ltd., Mumbai (98%)
- Iron Sulfide fused sticks for producing H_2S from Merck Pvt. Ltd., Mumbai
- Silicon high vacuum grease from RFCL Limited, New Delhi
- MDEA from Loba Chemie Pvt. Ltd., Mumbai (99%)

Estimation of sulfide content

- Sodium thiosulphate pentahydrate (purified) from Merck Pvt. Ltd. (≥99%)
- Potassium iodate GR from Merck Pvt. Ltd. (≥99.5%)
- Sodium hydroxide pellets (purified) from Merck Pvt. Ltd. (≥97%)
- Starch soluble GR from Merck Pvt. Ltd.
- Potassium iodide GR from Merck Pvt. Ltd. (99.8%)

Preparation of Organic Phase

- Toluene from RFCL Limited, New Delhi (≥99.5%)
- Benzyl chloride from Merck (India) Ltd., Mumbai (≥99%)
- Acetone from RFCL Limited, New Delhi (99.5%)

Catalyst

- ETPB from Sigma Aldrich, Mumbai.

3.2 Reaction Procedure for the Preparation of H_2S Rich Aqueous N - Methyldiethanolamine

For the preparation of H_2S-rich aqueous methydiethanolamine (MDEA), about 30- 35 wt% aqueous alkanolamine solution was firstly prepared by adding a desired amount of alkanolamine in distilled water. Secondly H_2S gas was organized in small scale in laboratory in Kipp's apparatus by reacting FeS sticks with 1M H_2SO_4.Then H_2S gas produced in the Kipp's apparatus and then bubble through this aqueous alkanolamines in a 250 ml standard gas bubbler as shown in below fig. 3.1. The H_2S that is unabsorbed by the Kipp's was sent to the atmosphere. 1 molar concentration of H_2SO_4 was made. The describe reaction carried out in Kipp's apparatus is as follows

The overall reaction is

$$Fes + H_2SO_4 \rightarrow H_2S + FeSO_4 \text{ (Exothermic)} \quad (3.1)$$

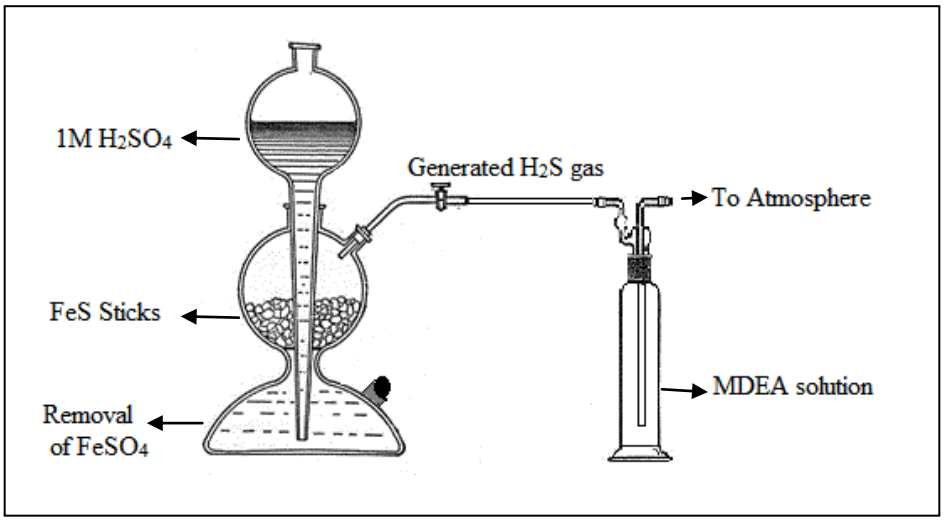


Figure 3.1 Kipp's apparatus for preparation of H_2S

The $FeSO_4$ was produced in the reaction and it was taken out from the bottom of kipp's apparatus. As the reaction of H_2S with alkanolamine is exothermic in nature (Kohl and Nielsen, 1997), so for the prevention of the formation of side products, the gas bubbler holding aqueous alkanolamine was placed in an ice water bath. Liquid samples were withdrawn at different interval after the gas bubbling was stopped and the samples were analyzed for sulfide content (Scott, 1966).The continuous process of gas bubbling was carried until the desired sulfide concentration was obtained in the aqueous alkanolamines. Iodometric titration method is used to determine the sulfide concentration.

3.2.1 Iodometric Titration Method:

Determination of Sulfide Concentration

The concentration of sulfide in aqueous alkanaolamine solution was determined by Iodometric titration method studied by Scott in 1966. Here, free iodine is liberated by reacting with oxidation agent in neutral or acidic medium with excess of potassium iodide (KI).

$$KI + \text{Oxidizing agent} \rightarrow I_2 \qquad (3.2)$$

A normal reducing agent sodium thiosulphate is prepared to titrate with liberated iodine. Starch solution is taken as an indicator which indicates the free iodine liberation through blue or violet colour. The change of iodine to iodide is recognized with colour change from blue to colourless (Sinha S., 2014). The steps of titration were given below.

Preparation of standard (0.025 M) KIO_3 solution**:**

5.3 gm of KIO_3 was taken and then dissolved in 1L of distilled water in a graduated volumetric flask.

Preparation of standard (0.1 M) sodium thiosulfate solution**:**

In 1L distilled water, 25 gm of $Na_2S_2O_3.5H_2O$ crystals was taken in a graduated volumetric flask. Around, 0.1 g of sodium carbonate or three drops of chloroform was weighted and taken to this solution for the reservation the solution to more than a few days.

Normalization of sodium thiosulfate solution by standard potassium iodate solution**:**

0.025M KIO_3 solution was taken as 25 mL and 1 gm (excess) of potassium iodide (KI) added to it. Additional 3 mL of 1 M sulfuric acid are made. In a burette, Thiosulfate solution was filled to titrate the liberated iodine (I_2) and continuously titrated the solution till colour changes from brown to pale yellow. After appearing pale yellow colour, solution was diluted to 200 mL with distilled water. . The preparation of starch solution was done by adding 0.2 g paste of starch in 100ml boiled water. After the cooling of starch solution for 10 min, 2.5 gm of KI was weighed and mixed to create the solution to 0.2%. Around a few drops of starch solution were added to the solution as an indicator and then again the titration was carried to the colour changes from blue to colourless. The chemical reactions involve in this titration method are given below.

$$KIO_3 + 5KI + H_2SO_4 \leftrightarrow 3I_2 + 3H_2O + 3K_2SO_4 \qquad (3.3)$$

$$2Na_2S_2O_3 + I_2 \leftrightarrow Na_2S_4O_6 + 2NaI \qquad (3.4)$$

Therefore, 1 mole of $KIO_3 \equiv$ 3×2 mole of $Na_2S_2O_3$.

$$\therefore \text{ Strength of Thiosulfate Solution} = \frac{6 \times \text{Strength of } KIO_3 \times \text{Volume of } KIO_3}{\text{Volume of Thiosulfate Consumed}}$$

Strength of sulfide concentration**:**

For the estimation of sulphide, hydrogen sulfide and soluble sulfides with potassium iodate in an alkaline medium is used. 15 cm^3 of standard (0.025M) potassium iodate solution was prepared in a conical flask and then add 10 cm^3 of sulfide solution. After that sodium hydroxide solution of amount 10 cm^3 of 10M was also added to mixture. The reaction mixture was then boiled mildly for about 10 minutes, cooled. 5 cm^3 of 5% KI solution and 20 $cm^3$of 4M sulphuric acid solution were added to solution after cooling of the mixture. The liberated iodine was titrated, which was equivalent to the unused potassium iodate, with a standard 0.1M sodium thiosulfate in the usual manner. As shown in the following reactions, the potassium iodate in the alkaline medium oxidizes the sulfide to sulfate. The sulfide solution requiring sufficiently high sulphide concentration, suitable dilution was prepared before the approximation of sulfide by above stated procedure.

$$44IO_3^- + 6OH^- + S^{2-} \rightarrow 4SO_4^{2-} + 4I^- + 6H_2O \qquad (3.5)$$

$$4 \text{ moles of } IO_3^- = 3 \text{ moles of } S^{2-}$$

$$\therefore H_2S \text{ Concentration} = \left[15 \times S_{iodate} - \frac{V_{thiosulfate} \times S_{thiosulfate}}{6}\right] \times \frac{3}{4} \times \frac{N_d}{10} \qquad (3.6)$$

Where, S_{iodate} = Strength of KIO_3

$V_{thiosulfate}$ = Volume of thiosulfate

$S_{thiosulfate}$ = Strength of thiosulfate

N_d = Number of times of dilution.

3.3 Equipment Set-Up

The reactions of CBC with H_2S-rich aqueous MDEA were distributed within the batch manner in a fully baffled mechanically agitated glass reactor of capability 250 cm^3 (6.5 cm i.d.). A 2.0 cm-diameter, six-bladed glass disk turbine impeller with facility of speed regulation was placed at a height of 1.5 cm from the bottom of the reactor. The impeller was placed to agitate the reaction. The batch reactor was equipped with four leg vertical baffle. The reactor was immersed in a constant temperature water bath whose temperature may be controlled at intervals ±1°C. The schematic diagram of the entire assembly is as shown in fig. 3.2.

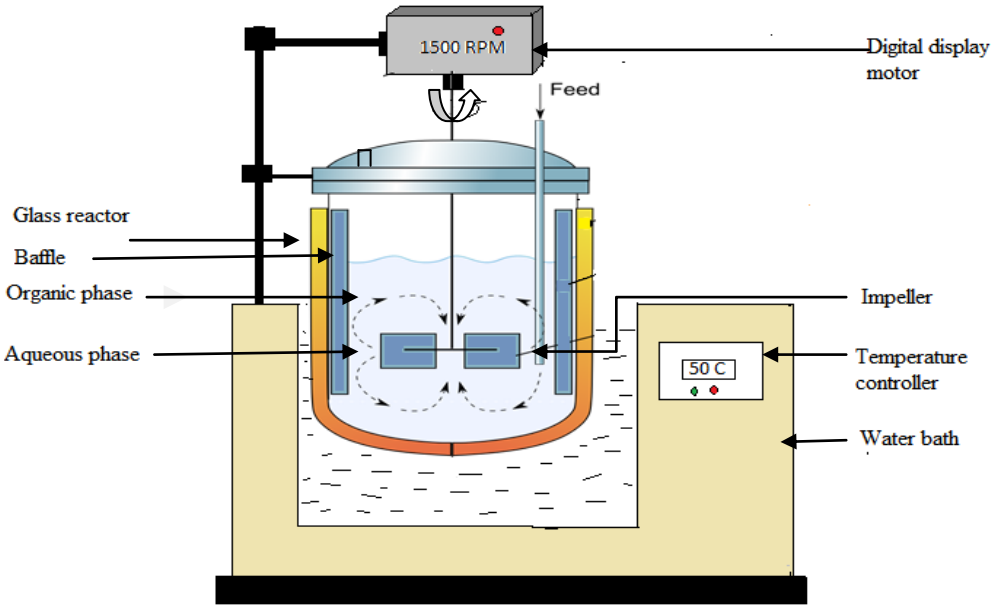


Figure 3.2: Schematic diagram of the batch reactor assembly

3.4. Reaction Procedure

The experimentation of the analysis, the three- necked batch reactor was introduced with a known amount of 50 cm^3 of aqueous phase containing known amount of sulfide concentration. The reactor was kept well agitated. If once steady state temperature appears, then reaction has stopped. After attainment of temperature, 50 cm^3 of the organic phase comprising measured quantity of organic reactant such as 4-chlorobenzyl chloride and known quantity of phase-transfer catalyst ETPB and toluene as a solvent is introduced within in the reactor. Now, the aqueous and organic solutions are mixed in a 250-cm^3 batch reactor wherever the reactor was

being immersed in an isothermal water bath, in order to initiate the reaction. The reaction mixture was stirred at a constant speed. At regular interval of time say 5-480 min, the regulation of stirred has stopped and permit the bi-phase to separate. After certain time of period, about $0.1cm^3$ of the organic sample from the organic layer was withdrawn. The collected was placed into the sample into the glass vials.

3.5 Analysis of Organic Phase:

The reaction of 4-chlorobenzylchloride with aqueous H_2S-rich MDEA were carried out in batch mode in presence of PT catalyst. The desired product bis(4-chlorobenzyl) sulfide and side product 4-chlorobenzyl mercaptan was detected in Gas Chromatography specially gas-liquid chromatography. A gas chromatograph (GC) is a chemical analytical technique used in industrial laboratory that measures the content of various components present in sample. The analysis performed by a gas chromatograph is called gas chromatography. GC is also a frequently used technique in many laboratories due to the detection of very small quantities. A broad variety of samples can be analysed to determine the composition of compounds which are sufficiently thermally stable and volatile. It involves a sample to be analysed is first injected into the head of the chromatographic column which is being vaporised after injection. The sample is transported through the column by the flow of inert which is gaseous mobile phase. Helium or unreactive gas like nitrogen is used as a Carrier gas. A very thin microscopic layer of liquid covered on surface of column is known as Stationary phase. Sample passes with carrier gas through column which is coated with stationary phase. When collaboration taking place between sample component and stationary phase then different component elute which is having different retention time from column. To determine the retention time, column detector is introduced.

Now Flame ionization detection (FID) is used to detect the organic compound. Two electrodes are located just outside the column with burning hydrogen/air flame. When organic sample is passed through the FID, it oxidise the organic molecules and produces the ions. That ions produce in GC-FID is electrically charged particles. The electrical signal is appeared in chromatograph in terms of peak.

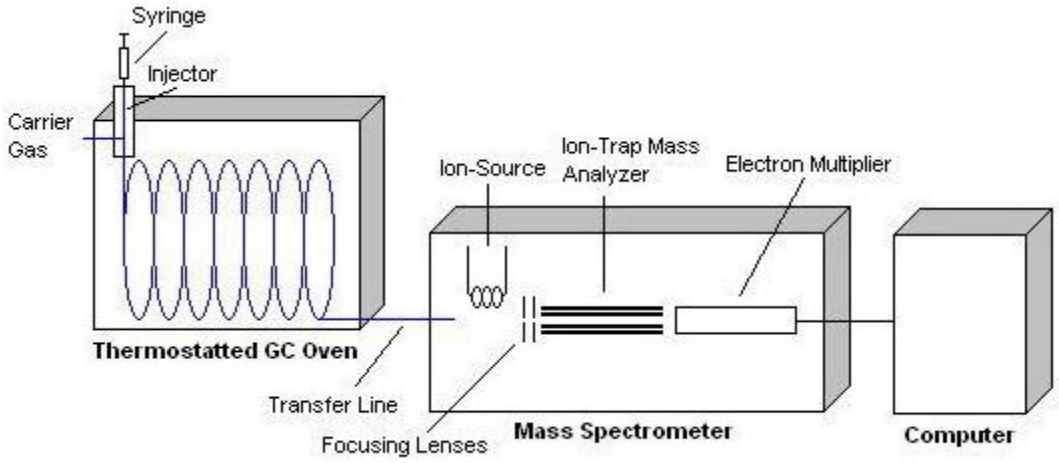


Figure 3.3: Block diagram of a typical GC-MS

For analyzing the compounds, a GC-MS from Agilent Technology model 7890B/5977A was used. The analyzing conditions are as follows

Table 3 MS PROGRAM

Injection Volume = 1µl

Inlet	**Column**	**Oven**
Heater = 300^0C	Agilent DB-5ms	Oven Temperature = 60^0C
Pressure = 11.724 psi	Flow = 1 ml/min	Maximum Oven Temperature = 324^0C
Purge Flow = 3ml/min	Pressure = 8.2317 psi	-
Mode = Split less	Holdup Time = 1.365 min	-
-	Agilent DB-5ms	-

	Rate (^{0}C/min)	Value (^{0}C)	Holdup Time (min)	Retention Time (min)
Initial		60	0.25	0.25
Ramp 1	100	150	0	1.15
Ramp 2	50	300	5	9.15

For GC-FID program, model 7890B is used for analysing the organic phase. The following table shows the FID program.

Table 4 FID PROGRAM

Injection Volume = 1µl

Inlet	**Column**	**Oven**	**Detector**
Heater = 200^0C	Agilent DB-5ms	Oven Temperature = 60^0C	Heater = 300^0C
Pressure = 15.345 psi	Carrier gas= nitrogen	Maximum Oven Temperature = 324^0C	Air Flow = 400 ml/min
Purge Flow = 3ml/min	Carrier gas Flow = 1.5 ml/min	Oven Temperature = 60^0C	H_2 Flow = 30 ml/min
-	Pressure = 15.345 psi	-	Make up Flow (N_2) = 25 ml/min
-	Holdup Time = 1.427 min		

	Rate (^{0}C/min)	Value (^{0}C)	Holdup Time (min)	Retention Time (min)
Initial		50	0	0
Ramp 1	30	170	0	4
Ramp 2	50	260	0	5.8
Ramp 3	10	280	1.2	9

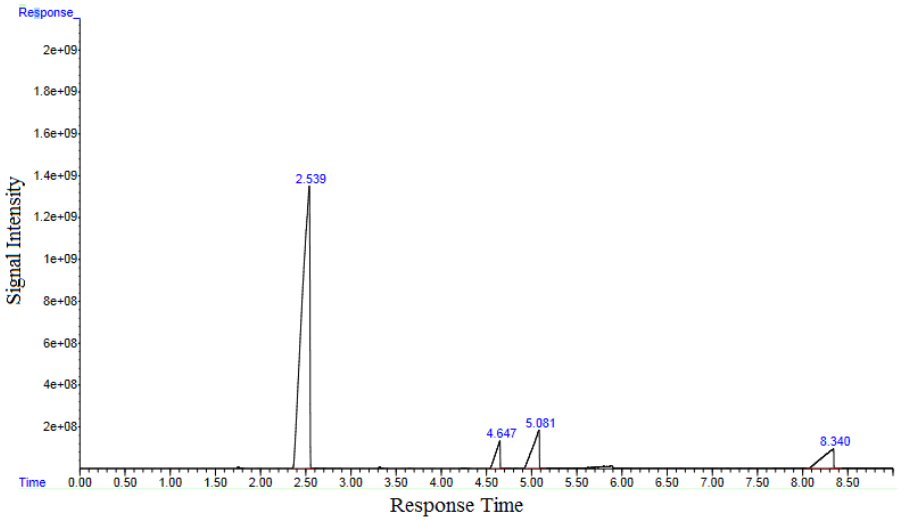


Figure 3.4 GC spectra of 4-chlorobenzyl chloride, 4-chlorobenzyl mercaptan and Bis-(4-chlorobenzyl) sulfide at 480 min of run

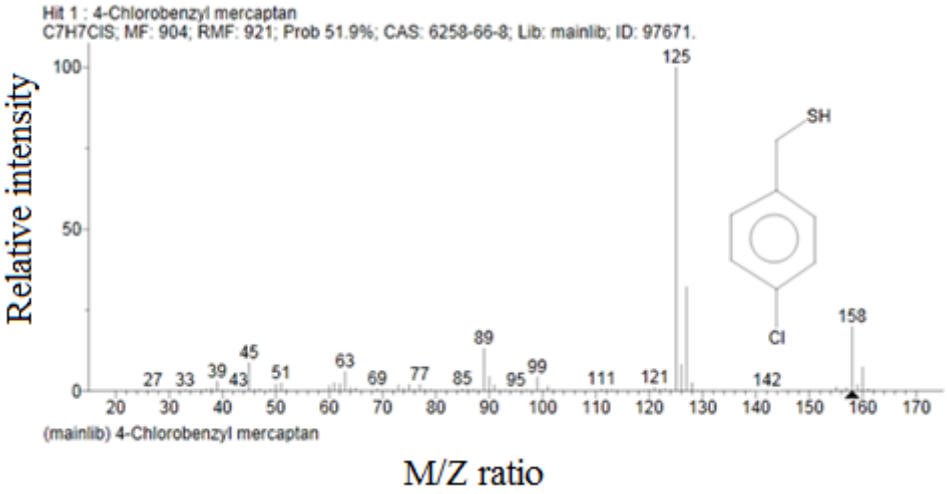


Figure 3.5: MS Spectra of the product 4-chlorobenzyl mercaptan

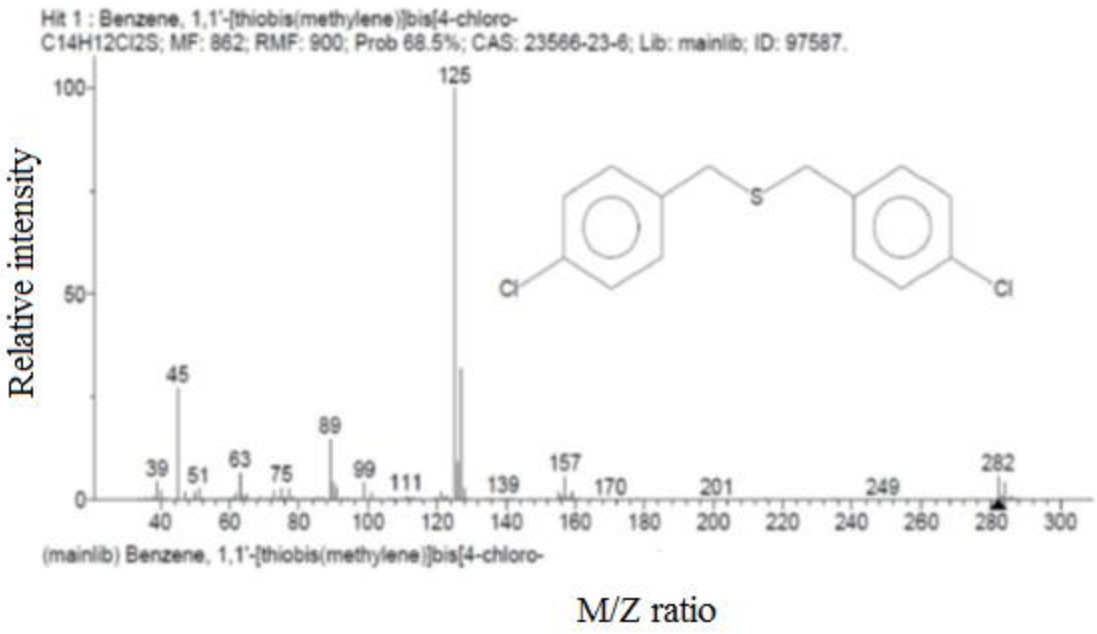


Figure 3.6 MS Spectra of the product Bis-(4-chlorobenzyl) sulfide

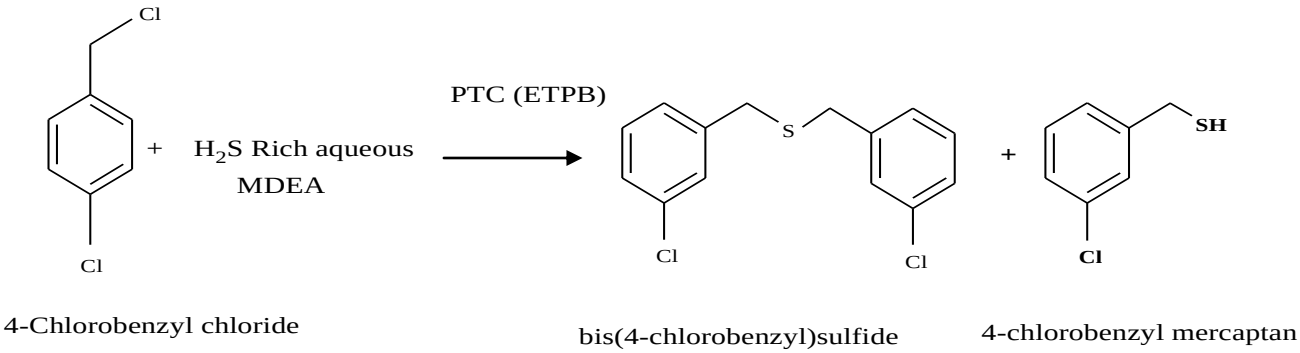
CHAPTER 4

SYNTHESIS OF BIS(4-CHLOROBENZYL) SULFIDE AND 4-CHLOROBENZYL MERCAPTAN

4. REACTION OF 4-CHLOROBENZYL CHLORIDE WITH H_2S-RICH AQUEOUS MDEA IN PRESENCE OF ETPB CATALYST UNDER LIQUID-LIQUID SYSTEM

4.1 INTRODUCTION

The reaction of 4-chlorobenzyl chloride with H_2S-rich MDEA solution can give fine chemicals like bis(4-chlorobenzyl) sulfide and 4-chlorobenzyl mercaptan as a product as per below scheme. In the current work, Phase transfer catalyst is used in this process to obtain high selectivity in short time. Here ethyltriphenylphosphonium bromide is use as phase transfer (PT) catalyst. The reaction is carried out in batch type under bi- phase conditions in presence of ETPB catalyst. The overall reaction may be represented by scheme 4.1



Scheme 4.1: Reaction of 4-chlorobenzyl chloride and H_2S-rich MDEA

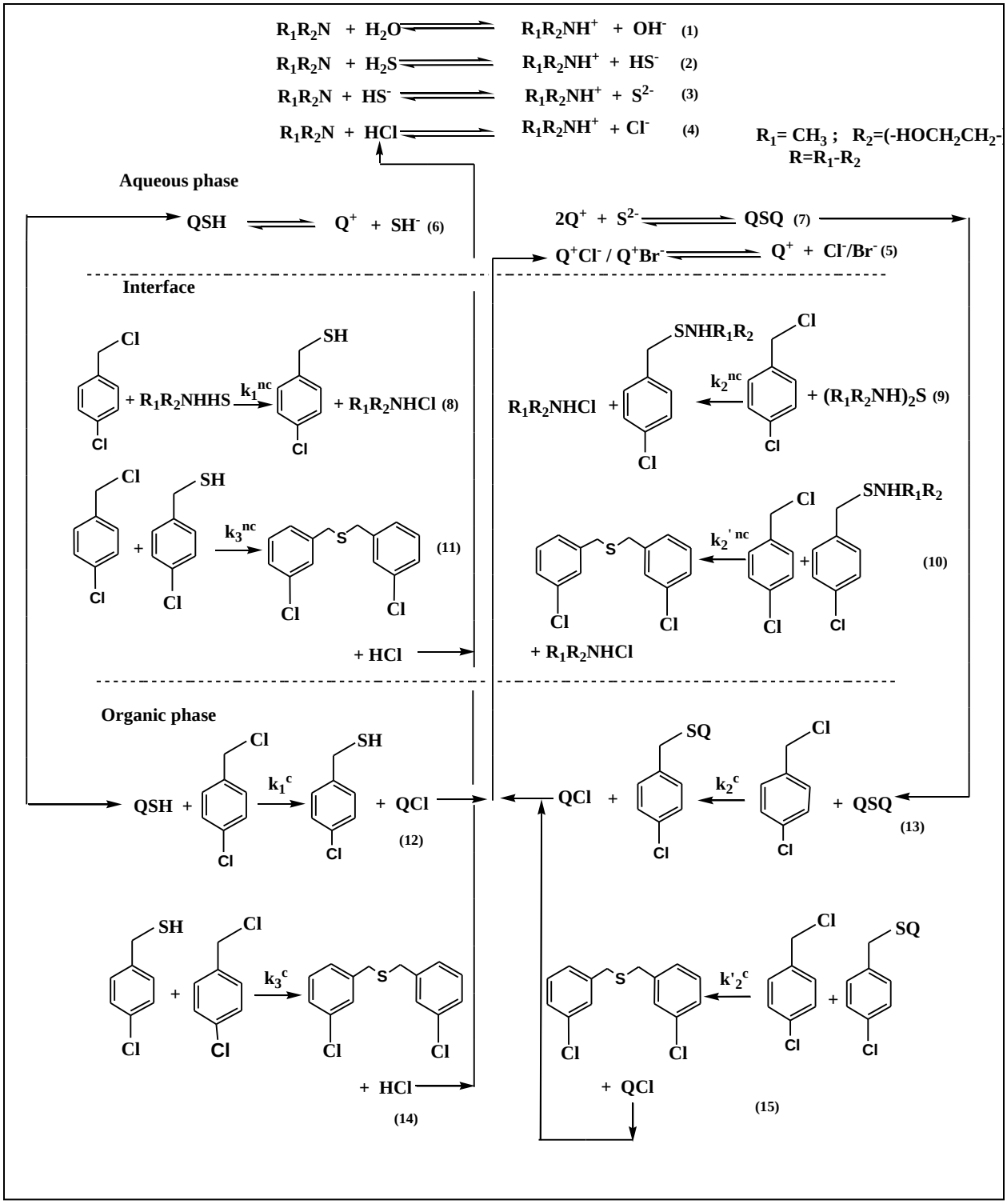
The products are detected from the organic mixture by gas-liquid chromatography(GLC).the selectivity of the two products bis(4-chlorobenzyl) sulfide and 4-chlorobenzyl mercaptan is well-defined as the fraction of 4-chloro benzyl chloride converted to particular product divided by the total fractional conversion of reactant. The rate and selectivity of desired product was enhances by changing different process parameters such as agitation speed, temperature, catalyst loading, reactant and sulfide concentration, MDEA concentration as discuss below. In order to determine the course of the reaction, the details study of effects of parameters on the reaction and suitable mechanism is recognized.

4.2 Mechanistic Investigation

4.2.1 Mechanism of Product Synthesis

Stark's (1971) and stark's and Liotta (1978) suggested mechanism called extraction mechanism which is used to explain the liquid-liquid phase transfer catalysis. Another mechanism was proposed for liquid-liquid by Dehmlow and Dehmlow (1983). Depending upon the lipophillic nature of catalyst being used, two different mechanisms are used to describe the course of the reaction. If PT catalyst having good distribution coefficient between the aqueous and organic phase so that it is not so lipophilic nature , extraction mechanism is used for this purpose such as tetrabutylammonium salt, dodecyltrimethylammonium, benzyltriethyammonium etc. whereas catalysts like tetrahexylammonium and trioctylmethyammonium salts having high lipophilic character that remain entirely in the organic phase, interfacial mechanism is used. Synthesis of bis(4-chlorobenzyl)sulfide and 4-chlorobenzyl mercaptan was accomplished by the reaction of chlorobenzyl chloride with hydrogen sulfide using ETPB catalyst, which can distribute itself between the two phase and ion exchange takes place between these two phases. Therefore the reaction mixture can be characterized by Stark's Extraction mechanism as shown in scheme 4.2.

In general, aqueous phase reactions are faster than organic reaction. For that reason there exists an ionic equilibrium with MDEA, H_2S and H_2O which gives active ions such as hydrosulfide, sulphide and hydroxide as shown in scheme. The active ions react with quaternary phosphonium salt producing ion pair like QOH, QSH and QSQ. In gas chromatography, chlorobenzyl alcohol chlorobenzyl amine was not identified due to their hydrophilic nature and can't transfer to organic phase in presence of catalyst (Wang and Tseng, 2003). Hence the hydrolysis of chlorobenzyl chloride under weak alkaline solution of aqueous MDEA is slow (Yadav et al., 2003). In aqueous phase, all amine molecules are present as cations, so that substitution reaction with CBC is impossible. From the parametric study we will discuss later, confirms that with increase in MDEA concentration in aqueous phase, there is an increase the selectivity of desired product. Therefore, only two active species QSH and QSQ are simultaneously formed and transferred to the organic phase due to lipophilic nature where the main reaction takes place.



Scheme 4.2: Synthesis of bis(4-chlorobenzyl) sulfide and 4-chlorobenzyl mercaptan

From the model of the reaction, it is seen that the sulfide ions present in the aqueous phase are first transfer the hydrosulfide ions (S^{2-} + 2 H_2O ↔ HS− + OH−) and then transferred to the

organic phase via phase transfer catalysis (Yadav et al., 2003). If only hydrosulfide ions are transferred, the reaction becomes series reactions and the desired product should form only by the reaction of CBM with CBC.

From the concentration profile plot 4.1 as shown below, the concentration of 4-chlorobenzyl mercaptan firstly increases and then slowly decreases with respect to time. Hence, 4-chlorobenzyl mercaptan is transformed to the high selectivity of bis(4-chlorobenzyl) sulfide. 4-chlorobenzyl chloride first reacts with 4-chlorobenzyl mercaptan and then form desired product bis(4-chlorobenzyl) sulfide and HCl as shown in scheme. Though HCl is strong acid that is prepared from weak acid like 4-chlorobenzyl mercaptan, the reaction mechanism is likely to be slow and it is ideal only in the presence of aqueous MDEA which reacts with hydrochloric acid to produce N-methyl- diethanolamine hydrochloride in the aqueous phase. The selective product increases with increasing time.

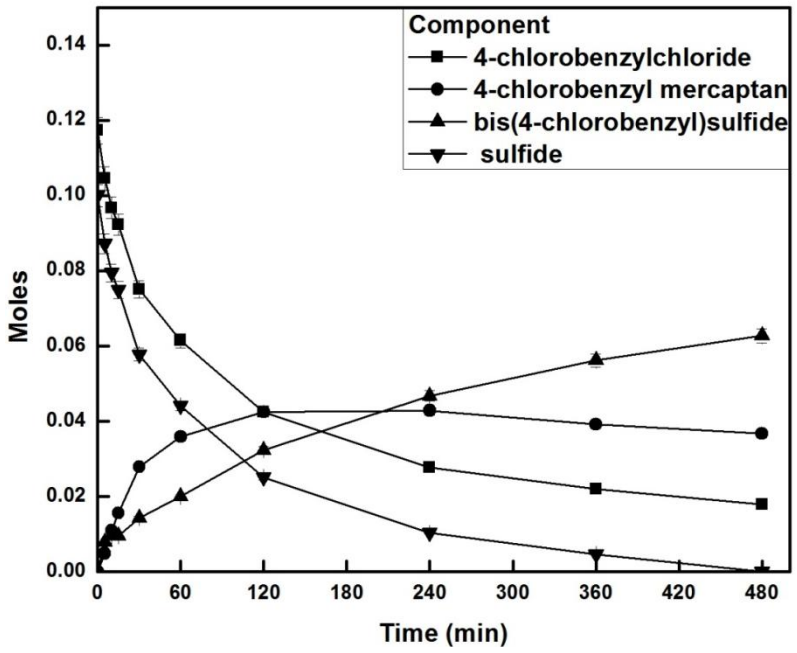


Figure.4.1: Concentration profile for the synthesis of Bis(4-chlorobenzyl)sulfide

Reaction conditions: Volume of organic and aqueous phase, 50×10^{-5} m^3 each; CBC concentration, 2.344 kmol/m^3; ETPB concentration, 0.04 kmol/m^3 organic phase; Temperature, 323K; Speed of agitation, 1500 rpm; MDEA Concentration, 3.05 kmol/m^3; Sulfide concentration, 2.0 kmol/ m^3.

At the interface, active catalyst, aqueous phase reactions and extraction of catalysts are considered as equilibrium. The overall rate of reaction in presence of catalyst has two contributions. There are: non- catalytic and catalytic.

4.2.1 Non-Catalytic Contribution:

Methyldiethanolamine Sulfide $(R_1R_2NH)_2S$ and Methyldiethanolamine hydrosulfide (R_1R_2NHHS) are made in an aqueous phase and they are not soluble in organic phase. In non-catalysed reaction, they are likely to react with CBC at aqueous-organic boundary to produce bis(4-chlorobenzyl) sulfide and CBM respectively. The non-catalytic reactions at the interface are represented by equations 8-11.While nucleophilic substitution reactions are normally 2^{nd} order reaction, hence the reaction between CBC and $(R_1R_2NH)_2S$ are expected to form an intermediate $C_6H_5CH_2SNH\ R_1R_2$ which promote to react with CBC to produce bis(4-chlorobenzyl) sulfide. Some CBM again reacts with CBC to give high selectivity of desired product bis(4-chlorobenzyl) sulfide.

4.2.2 Catalytic Contribution:

In catalytic pathway**,** phase transfer phosphonium cation Q^+ exchanges ion with Methyldiethanolamine sulfide ($(R_1R_2NH)_2S$) and hydrosulfide (R_1R_2NHSH) to form catalyst ions pairs QSQ and QSH in organic phase, again react with organic reactant CBC to give bis(4-chlorobenzyl) sulfide and 4-chlorobenyl mercaptan respectively as shown in equations (12-15). Again bis(4-chlorobenzyl) sulfide was produced via development of intermediate product $ClC_6H_5CH_2SQ$ which further combine with CBC to give desired product bis(4-chlorobenzyl) sulfide.

4.4 RESULTS AND DISCUSSION

Reaction of 4-Chlorobenzylchloride with Aqueous MDEA under Liquid-Liquid mode using PT catalyst

In this study, the reaction between CBC with H_2S rich MDEA is performed under liquid-liquid Phase transfer catalyst like ETPB at different reaction conditions to increase the selectivity of desired product. This study is made to develop a state-of-the-art process to produce commercially important chemicals by utilization of hazardous hydrogen sulfide and reduce the reactor volume as well as reduce the loss of solvent. The effects of various parameters on the rates of reaction of the 4-chlorobenzyl chloride are studied and reported below.

4.4.1 Effect of Speed of Agitation:

The effect of speed of agitation was studied to determine the influence of mass transfer resistance by varying the speed of agitation in the range of 0-2000 rev/min in the presence of phase transfer catalyst, ETPB. At 500 rpm, the conversion was achieving 62% and without using agitator, it was achieved only 8%. As observed from the figure, the variation of reaction rate with speed of agitation is so small that indicates the reactor system is free from mass transfer resistance. Figure 4.2 shows the conversion of 4-chlorobenzyl chloride with time which was found to be practically the same at 1500 and 2000 rpm. There is no effect on the conversion if the speed of agitation is increase. Therefore reactions may be considered as kinetically controlled reaction. All other experiments were performed at 1500 rpm in order to get maximum rate and to avoid the effects of mass transfer resistance on the reaction kinetics.

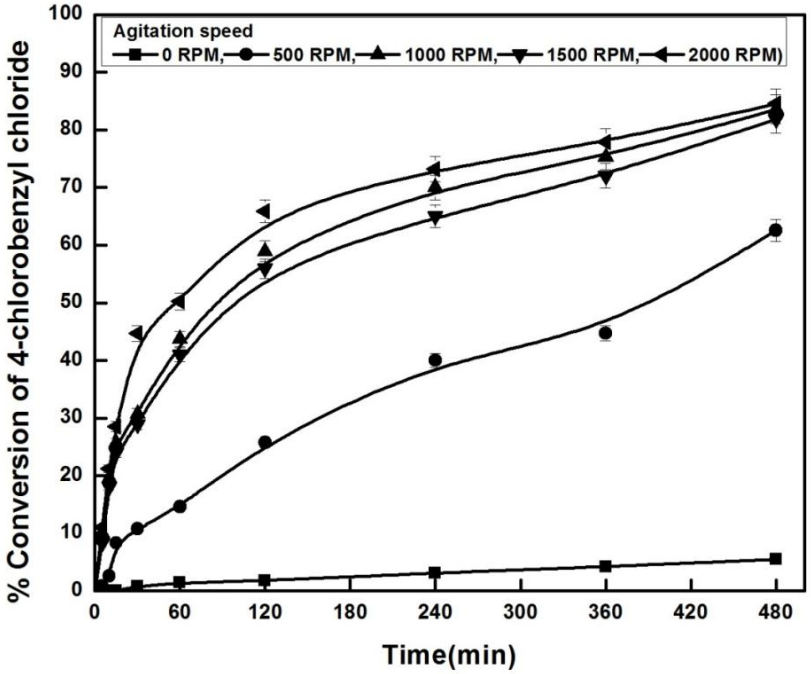


Figure 4.2: Effect of agitation speed on CBC conversion

Reaction condition: Volume of organic and aqueous phase, 50×10^{-5} m^3 each; CBC concentration, 2.34 kmol/m^3; ETPB concentration, 0.04 kmol/m^3 organic phase; Temperature, 323K; Speed of agitation, 0, 500, 1000, 1500, 2000 rpm; MDEA Concentration, 3.05 kmol/m^3; Sulfide concentration, 2.0 kmol/ m^3

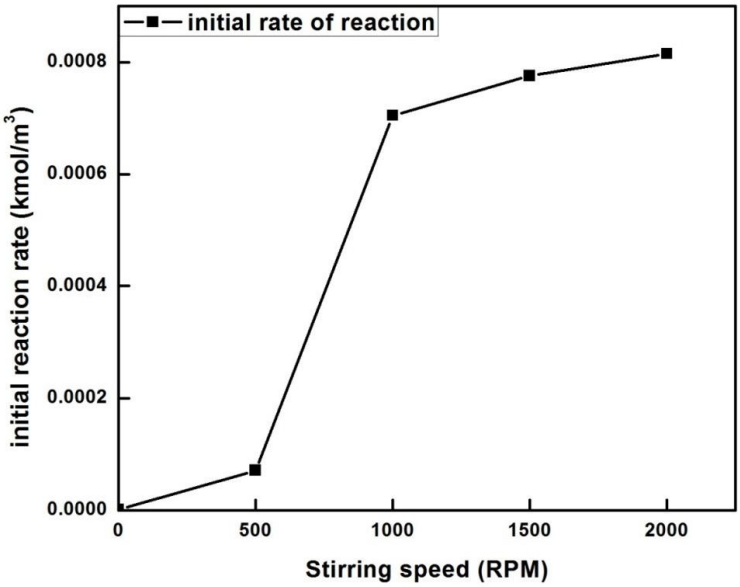
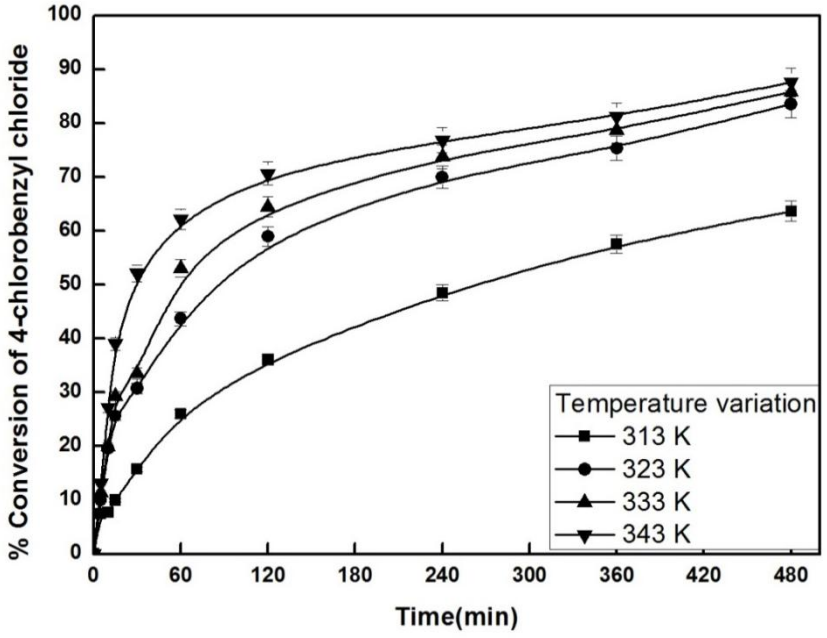


Figure 4.3: Initial rate vs speed of agitation (Same reaction conditions as above fig)

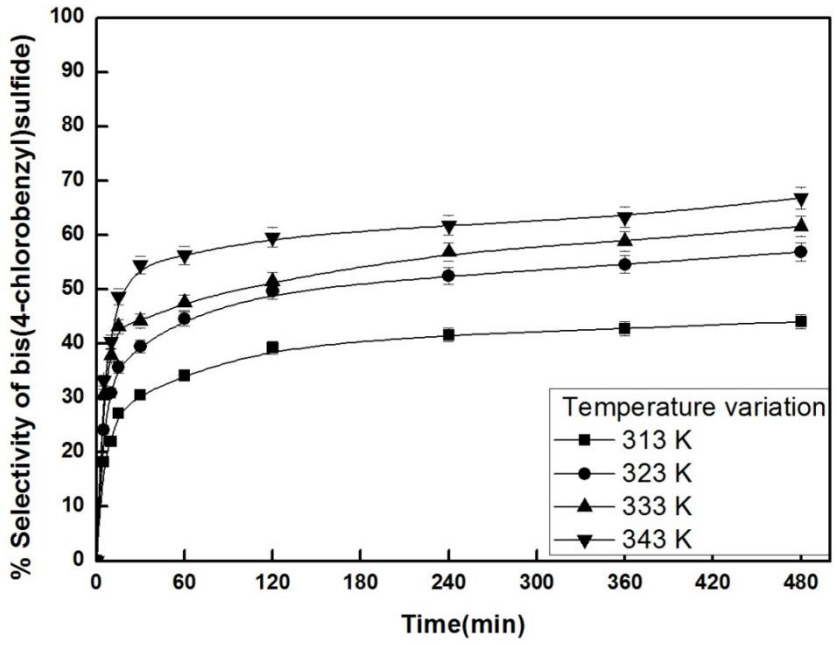
4.4.2 Effect of Temperature*:*

The influence of temperature on the rate of reaction of 4-chlorobenzyl chloride with H_2S rich MDEA was examined in different choice of 313-343 K at existence of PTC. As it is observed from the graph 4.3, the rate of reaction increases with increasing temperature as well as the conversion increases substantially with increase in temperature as expected.

An initial rate of reaction of CBC was calculated at different temperature conditions and to determine the activation energy, Arrhenius plot of logarithm (Initial Reaction Rate) Vs 1/T (K^{-1}) was made as shown in figure. The apparent activation energy for the reaction of CBC was found from the slope of straight line to be 11.28 kJ/mol. The observed activation energy indicates that reaction is kinetically control.



(a)



(b)

Figure 4.3: Effect of Temperature on (a) CBC conversion (b) Bis(4-chlorobenzyl) sulfide Selectivity

Reaction conditions: Volume of organic and aqueous phase, 50×10^{-5} m^3 each; CBC concentration, 2.34 kmol/m^3; ETPB concentration, 0.04 kmol/m^3 organic phase; Temperature, 313,323,333,343K; Speed of agitation, 1500 rpm; MDEA Concentration, 3.05 kmol/m^3; Sulfide concentration, 2.0 kmol/ m^3.

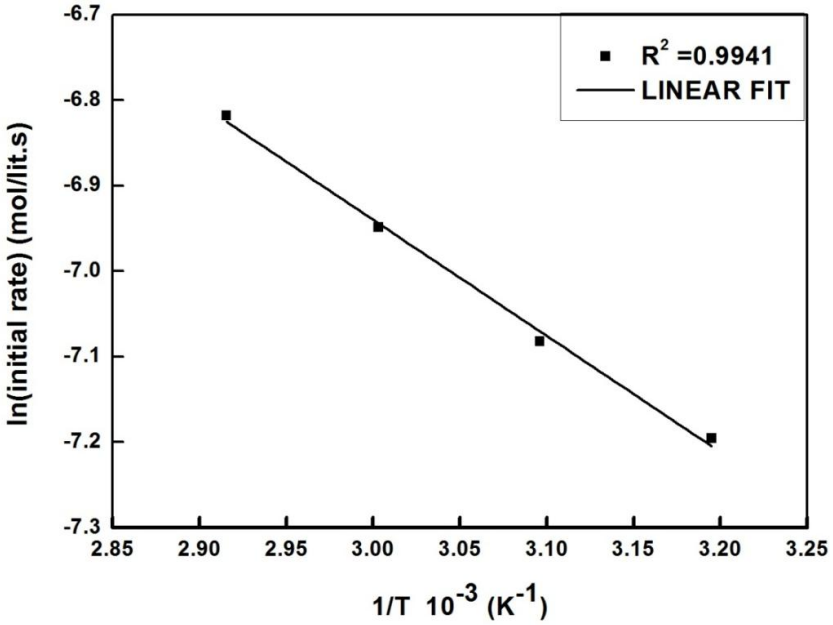


Figure 4.4: Arrhenius plot

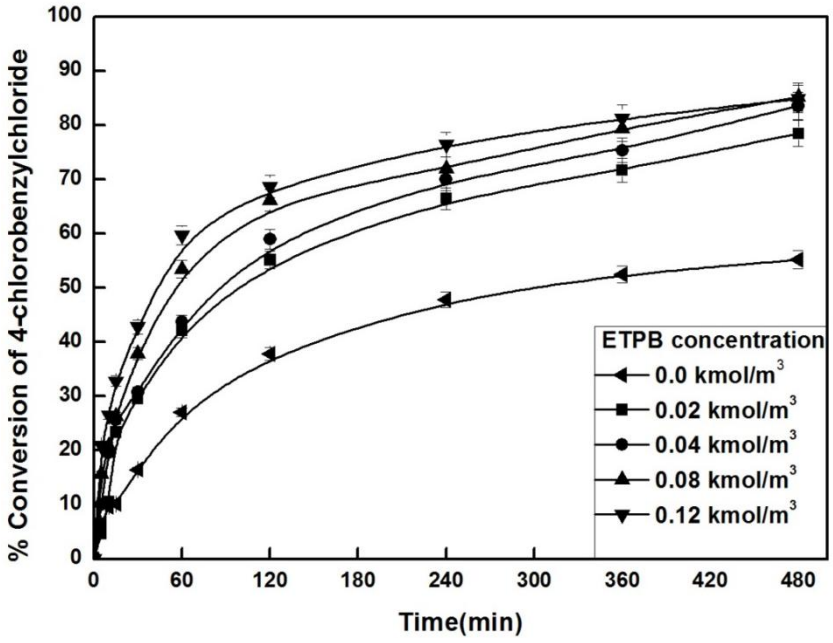
4.4.3 Effect of Concentration PTC (ETPB)

The outcome of different PTC concentration was considered in the concentration range of 0.00-0.12 kmol m^{-3} of organic phase as shown in figure 4.5 to know the conversion effect. The work was also showed in absence of catalyst. If the catalyst concentration increases, the conversion of 4-chlorobenzyl chloride and reaction rate also increases. From the graph, the conversion of bis(4-chlorobenzyl) sulfide achieved 55 % without using catalyst and in the presence of catalyst, conversion of more than 85% was achieved after 480 min of the reaction run under identical experimental conditions. This specified that the phase transfer catalyst enhances the rate of reaction under investigation. Figure illustrated the effect of concentration catalyst. The conversion of CBC becomes constant at certain concentration of catalyst which implies that mass transfer of active ions reaches a maximum value. Figure also shows the selectivity curves with respect to time. The selectivity of bis(4-chlorobenzyl) sulfide increases with an increase in catalyst concentration and simultaneously 4-chlorobenzyl mercapatan decreases with catalyst concentration.

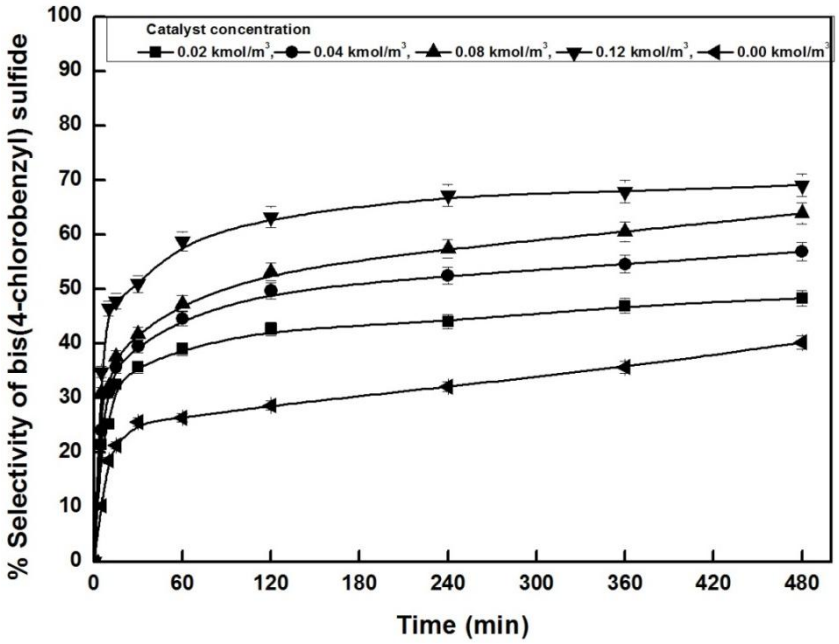
In liquid-liquid biphasic system, the overall rate of reaction was proposed by transformation of ions from aqueous to organic phase. The anions present in aqueous phase HS^- and S^{2-} is facilitated in presence of PTC and the reaction becomes organic phase limited. The aqueous

phase first react with quaternary phosphonium cation [Q+] to form ion pairs such as QHS and QSQ and migrates to the organic phase and then react with CBC to form bis(4-chlorobenzyl) sulfide. Here with increase in catalyst loading, more quantity of Q^2S ion pair made. Therefore selectivity of desired product is formed with increase in catalyst.

The enhancement factor defined as the ratio of reaction rate in presence of ETPB catalyst to that rate in absence of ETPB catalyst at constant conversion of CBC for different ETPB catalyst concentration. From the table, it is seen that the enhancement factor increases with increasing catalyst concentration. The enhancement factor of 3.44 was maximum rate which was observed with catalyst concentration of 0.12 kmol/m^3 of organic phase.



(a)



(b)

Figure 4.5: Effect of Catalyst concentration on (a) CBC Conversion (b) bis(4-chlorobenzyl) sulfide Selectivity:

Reaction conditions: Volume of organic and aqueous phase, 50×10^{-5} m^3 each; CBC concentration, 2.34 kmol/m^3; ETPB concentration, 0,0.02,0.04,0.08,0.12 kmol/m^3 organic phase; Temperature, 323K; Speed of agitation, 1500 rpm; MDEA Concentration, 3.05 kmol/m^3; Sulfide concentration, 2.0 kmol/ m^3.

Table 5: Effect of catalyst loading on initial rate of reaction and enhancement factor

Concentration of ETPB (kmol/m^3 org phase)	**Initial reaction rate (kmol/m^3s) × 10^4 at 5% Conversion**	**Enhancement Factor**
0	0.57	-
0.02	3.83	0.7
0.04	7.75	1.4
0.08	14.47	2.5
0.12	19.56	3.4

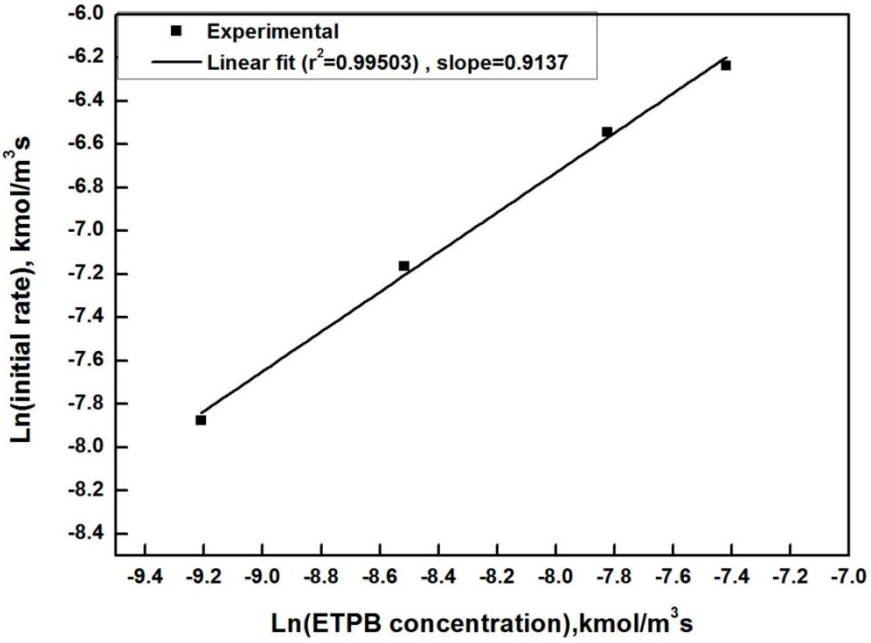
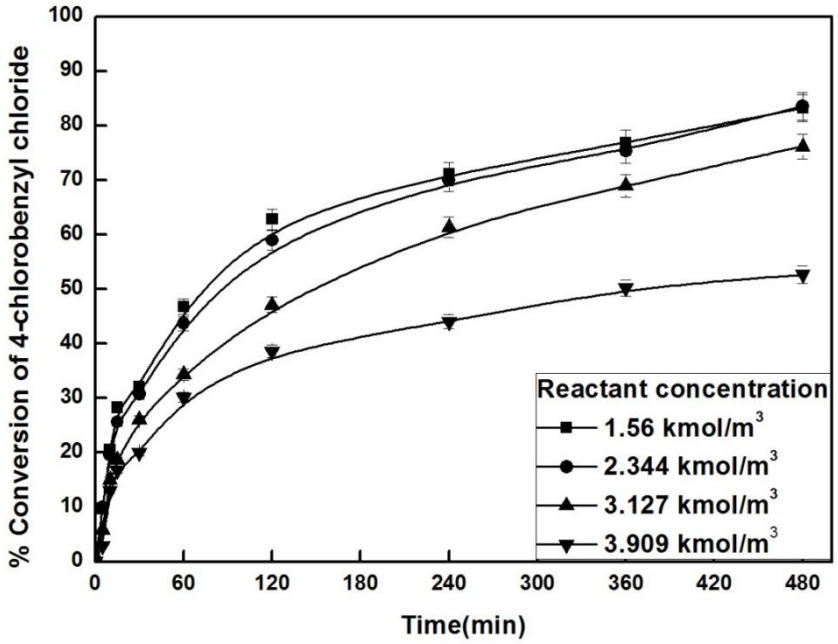


Figure 4.6: Reaction order with respect to catalyst concentration

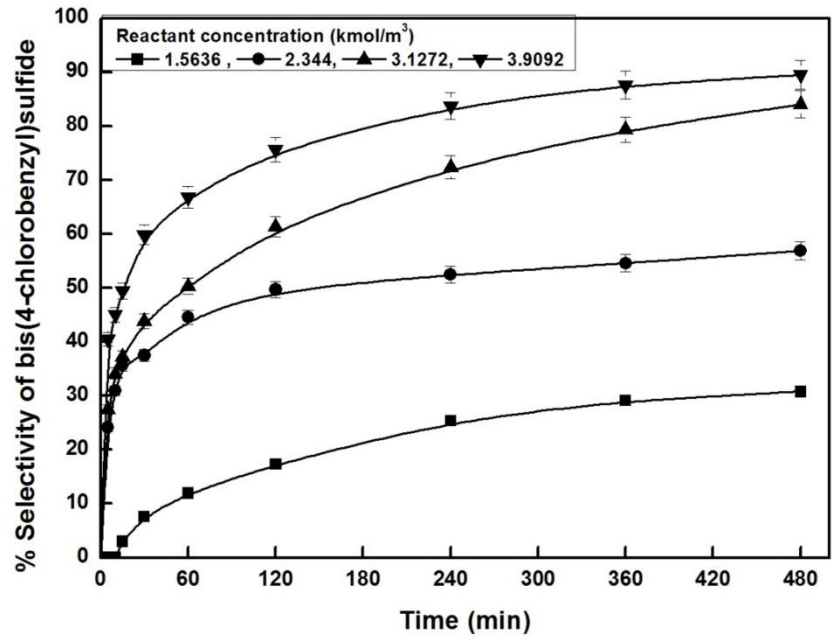
4.4.4 Effect of 4-Chlorobenzyl Chloride Concentration:

The 4-chlorobenzyl chloride (CBC) concentration was studied 1.56-3.909 kmol/m^3 in organic phase at constant sulphide concentration as shown in graph.it is evident from the graph that an increase in CBC reactant concentration decrease the conversion of CBC. This is due to the fact that limited quantity of sufides, S^{2-} and HS^- present in aqueous phase. The conversion of CBC concentration 1.56 kmol/m^3 is achieved 83.19% whereas at 3.909 kmol/m^3 concentration is 52.65% after 480 min of reaction run at same conditions.

The bis(4-chlorobenzyl) sulfide selectivity was noticed at high CBC as given in figure.89.4% selectivity was found with 3.909 mole at 480 min of the reaction time. From the graph of selectivity of bis(4-chlorobenzyl) sulfide versus CBC conversion (Fig. 4.8), it is witnessed that there is a sudden increase of curve with increase in the CBC concentration. As the reaction prominent to the conversion of 4-chlorobenzyl mercaptan is comparatively fast than the formation of bis(4-chlorobenzyl)sulfide. At low concentration of 4-chlorobenzyl chloride, the small quantity of reactant presents in the reaction mixture is produce desired product, which results in low selectivity of DBS. Hence to get appreciable conversion as well as selectivity 2.344 is considered to be optimum condition for further study.



(a)



(b)

Figure 4.7: Effect of CBC Concentration on (a) CBC Conversion (b) Bis(4-chlorobenzyl) sulfide Selectivity

Reaction conditions: Volume of organic and aqueous phase, 50×10^{-5} m^3 each; CBC concentration, 1.56, 2.34, 3.127, 3.909 kmol/m^3; ETPB concentration, 0.04 kmol/m^3 organic phase; Temperature, 323K; Speed of agitation, 1500 rpm; MDEA Concentration, 3.05 kmol/m^3; Sulfide concentration, 2 .0 kmol/ m^3.

From the plot of selectivity of bis(4-chlorobenzyl) sulfide and conversion of 4-chlorobenzyl chloride (figure 4.8), it is evident from the plot that there is an increase of slope of the curve with an increase in CBC concentration. Subsequently the reaction converting to the formation of 4-chlorobenzyl mercaptan is accelerated as compare to the desired product. At low 4-chlorobenzyl chloride concentration, there will be inadequate amount of CBC present to produce low selectivity bis(4-chlorobenzyl) sulfide.

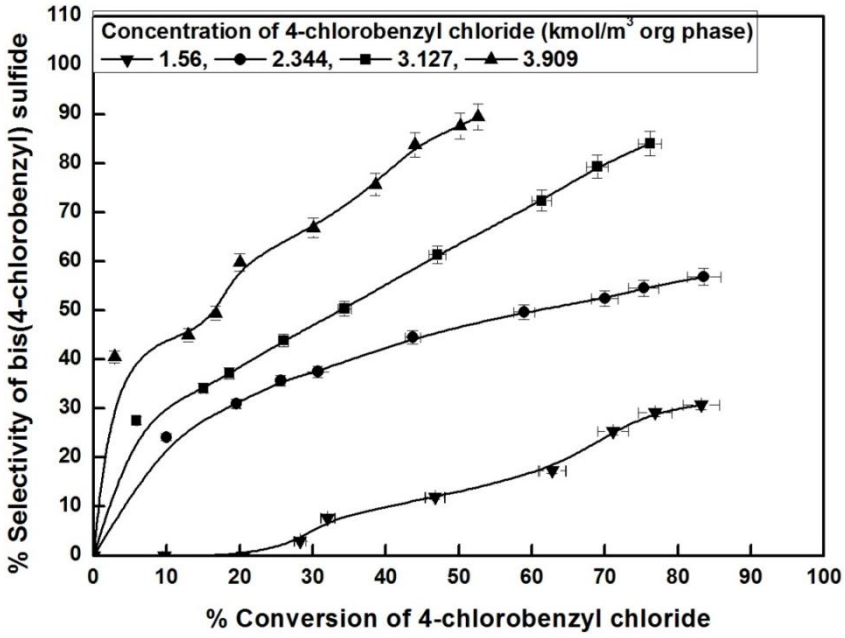
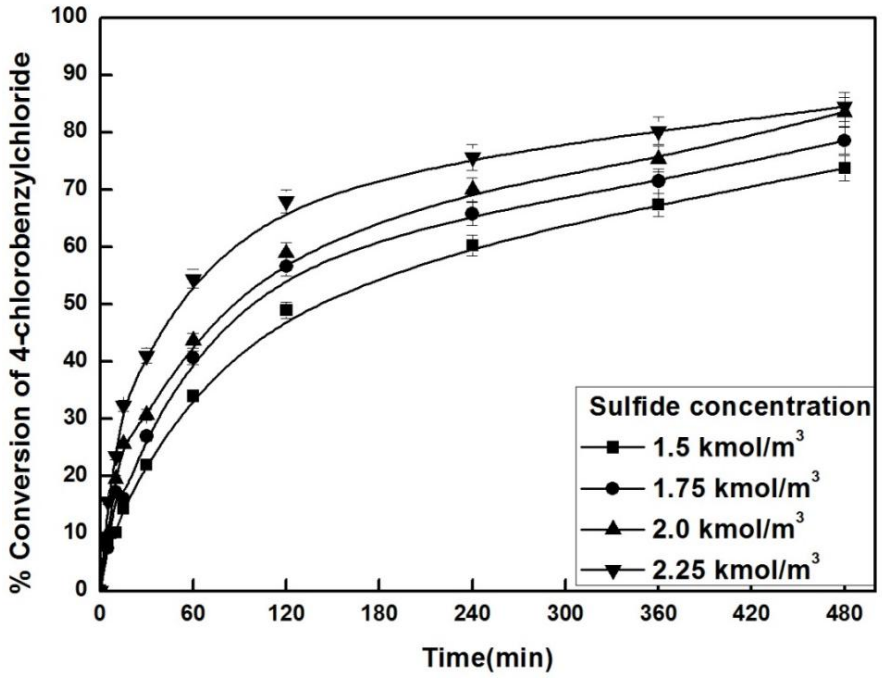


Figure 4.8: Relationship between conversion of CBC and selectivity of bis(4-chlorobenzyl) sulfide under different chlorobenyl chloride concentration

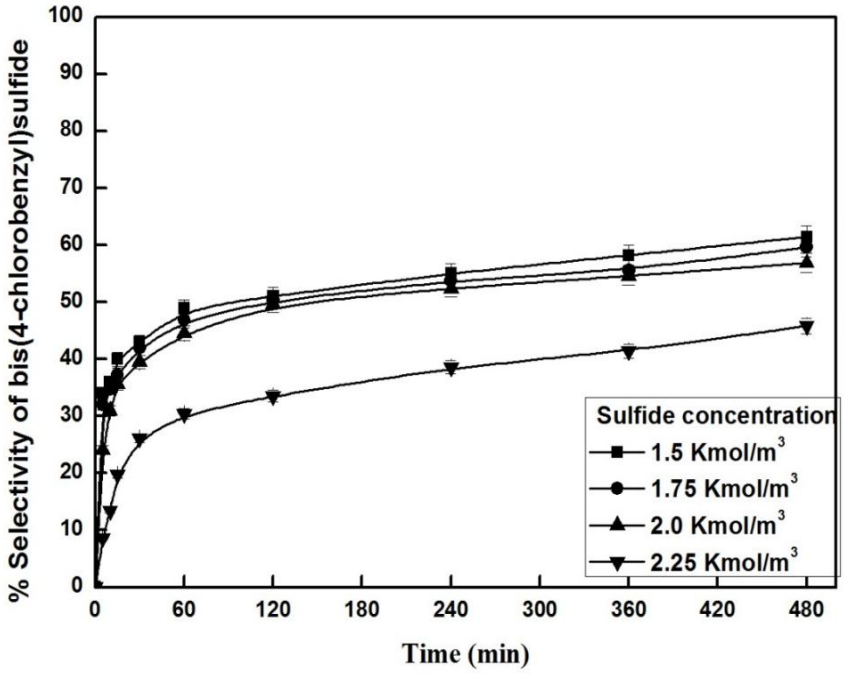
Reaction conditions: Volume of organic and aqueous phase, 50×10^{-5} m^3 each; CBC concentration, 1.56,2.34,3.127,3.909 kmol/m^3; ETPB concentration, 0.04 kmol/m^3 organic phase; Temperature, 323K; Speed of agitation, 1500 rpm; MDEA Concentration, 3.05 kmol/m^3; Sulfide concentration, 2 .0 kmol/ m^3.

4.4.5 Effect of Sulfide Concentration:

The influence of sulfide concentration on synthesis of bis(4-cholrobenzyl) sulfide was investigated by using different concentration of sulphur concentration in aqueous phase at constant MDEA concentration of 3.04 kmol/m^3. The study of sulphide effect was varied from 1.5 to 2.25 kmol/m^3.with increase in sulphide ion HS- in aqueous phase increases the conversion of 4-chlorobenzyl chloride and was achieved 89% after 480 min of reaction at similar conditions. However another trend was studied for selectivity of bis(4-chlorobenzyl) sulfide. From the figure 4.10, it is seen that the selectivity of bis(4-chlorobenzyl) sulfide increase with decrease in sulphide concentration. A selectivity of bis(4-chlorobenzyl) sulfide of about 61% was found with concentration of after 480 min under similar conditions. As the concentration of sulfide increases, selectivity of bis(4-chlorobenzyl) sulfide decrease. MDEA do not take part in the reaction of 4-chlorobenzyl chloride, it only affect the ionic equilibrium among MDEA, H_2S and H_2O resulting two active anions S^{2-} and HS^-.



(a)



(b)

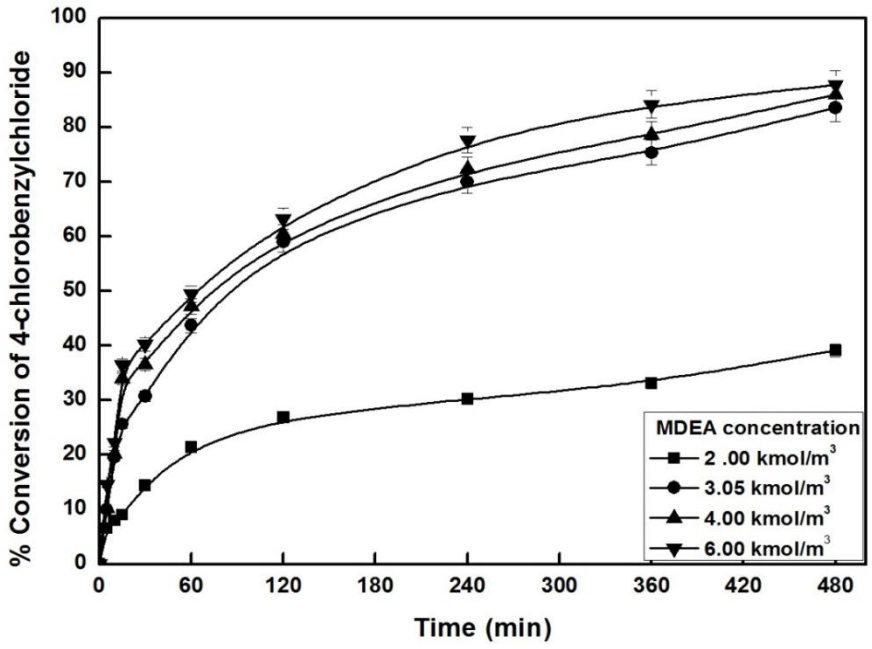
Figure 4.9: Effect of Sulfide Concentration on (a) CBC Conversion (b) Bis(4-chlorobenzyl) sulfide Selectivity

Reaction conditions: Volume of organic and aqueous phase, 50×10^{-5} m^3 each; CBC concentration, 2.34 kmol/m^3; ETPB concentration, 0.04 kmol/m^3 organic phase; Temperature, 323K; Speed of agitation, 1500 rpm; MDEA Concentration, 3.05 kmol/m^3; Sulfide concentration, 1.5, 1.75, 2.0, 2.25 kmol/ m^3.

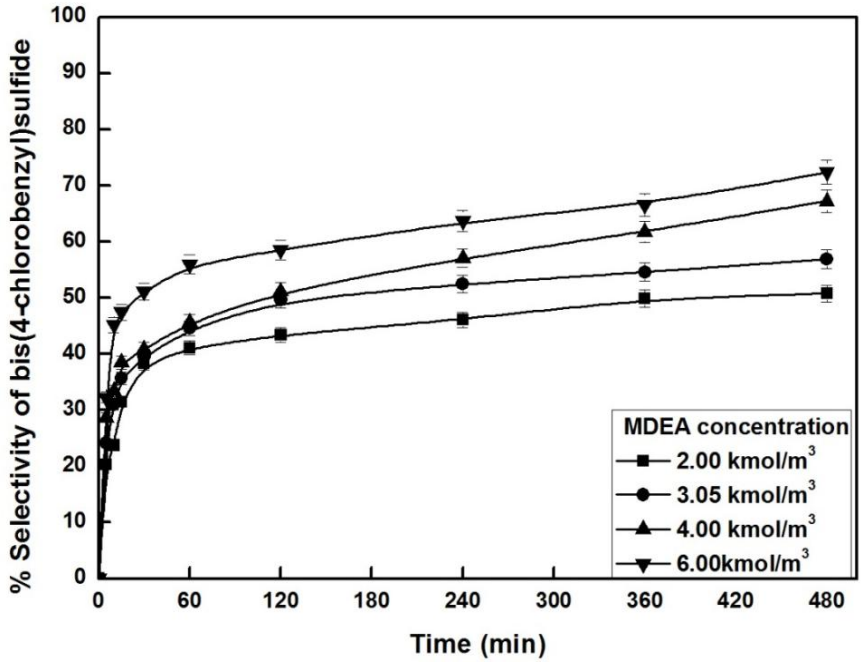
4.4.6 Effect of MDEA Concentration:

The MDEA concentration in the aqueous phase was ranged keeping initial sulfide concentration of 2.0 kmol/m^3. To know the conversion, the aqueous sulfide of different MDEA concentrations were prepared by taking 30 cm^3 of known aqueous sulfide and MDEA concentrations and then add different concentrations of aqueous MDEA and distilled water to get 50 m^3 aqueous solution. From the graphs, it was seen that increase in MDEA concentration in aqueous phase conversion as well as selectivity also increases. Therefore, the 4-chlorobenzyl mercaptan decreases with increase in MDEA at fixed conversion of CBC.

In the system, MDEA doesn't take part in the reaction as shown in scheme. MDEA acts as an absorbent for H_2S absorption. It plays an important role for equilibrium among MDEA, H_2S and H_2O in aqueous phase resulting two active anions S^{2-} and HS^-. With increase in MDEA, concentration of sulfide ion also increases which results high selectivity of product. From the scheme, it is noticed that one mole of sulfide reacts with two mole of moles of 4-cholrobenzyl chloride and form one mole of bis(4-chlorobenzyl) sulfide. On the other hand one mole of 4-chlorobenzyl chloride reacts with one sulfide to form 4-chlorobenzyl mercaptan. At constant sulfide concentration, conversion increases with increasing MDEA concentration. This is due to higher selectivity of bis(4-chlorobenzyl) sulfide at high MDEA. Hence it is easy to be proved the existence of two different reactions by varying the MDEA concentration with constant sulfide concentration.



(a)



(b)

Figure 4.10: Effect of MDEA Concentration on (a) CBC Conversion (b) Bis(4-chlorobenzyl) sulfide Selectivity

Reaction conditions: Volume of organic and aqueous phase, 50×10^{-5} m^3 each; CBC concentration, 2.344 kmol/m^3; ETPB concentration, 0.04 kmol/m^3 organic phase; Temperature, 323K; Speed of agitation, 1500 rpm; MDEA Concentration, 2.00, 3.05, 4.00, 6.00 kmol/m^3; Sulfide concentration, 2.0 kmol/ m^3.

CHAPTER 5

SUMMARY AND CONCLUSIONS

5. SUMMARY AND CONCLUSIONS:

The reaction of an organic compound such as 4-chlorobenzyl chloride with hydrogen sulphide results in the formation of diaryl sulfides. The extensive use of diaryl sulfide is the pharmaceutical industry, antiwear motor oil additives, extreme pressure lubricants, stabilization of photographic emulsions, in refining and recovery of important metals and anti-corrosive paints. Present work was reported the synthesis of diaryl sulfide by phase transfer catalysis. The reaction was investigated in the existence of phosphonium based catalyst. Ethyltriphenyl-phosphonium bromide (ETPB) is used as phase transfer catalyst due to its chemical stability and thermal stability. The influence of process parameters like agitation speed, catalyst loading, reactant concentration, temperature effect, MDEA concentration and elemental sulphur loading were studied to determine the conversion, selectivity, and reaction rate. One can selectivity prepare either bis(4-chlorobenzyl) sulfide and 4-chlorobenzyl mercaptan using same reagents only by selecting suitable experimental conditions. A high 4-chlorobenzyl chloride concentration, high MDEA concentration and long reaction time lead to the selective production of bis(4-chlorobenzyl) sulfide. The selectivity of bis(4-chlorobenzyl) sulfide was about 89.47%.

The reaction is intrinsically kinetic controlled above the stirring speed of 1000 rpm. The two stage reaction of 4-chlorobenzyl chloride with H_2S-rich MDEA is considered to be mass transfer controlled with apparent activation energy of 11.28 kJ/mol.

A complex mechanism like extraction mechanism involves in this biphasic liquid-liquid system. An ionic equilibrium such as MDEA, H_2S and H_2O forms sulphide (S^{2-}) and hydrosulfide (HS^-) ion in aqueous phase was recognized. The two active species Q^+SH^- and $Q^+S^{2-}Q^+$ are generated in aqueous phase in presence of phase transfer catalysis and migrated to organic phase. The organic phase containing 4-chlorobenzyl chloride react with these active catalysts to produce bis(4-chlorobenzyl)sulphide and 4-chlorobenzyl mercaptan respectively.

From the proposed study it is observed that PT catalyst is a nice alternative to the traditional sulphur recovery process. This process produces commercially fine chemicals along with elemental sulphur in a cost effective way. Therefore, the process might to be considered as alternative to the Claus Sulphur Recovery Process, Wet Oxidation LO-CAT Process and CrystaSulf.

CHAPTER 6

FUTURE SCOPE

6. FUTURE SCOPE:

An efficient study was conducted to produce commercially important fine chemicals via biphasic phase transfer catalysis (L-L PTC) reaction of 4-chlorobenzyl chloride and hydrogen sulfide rich aqueous alkanolamine solution. The present investigation deals with the conversion of harmful chemical like hydrogen sulfide to nontoxic elemental sulfur. Further investigation could be directed in following:

6.1 Finding out the Effect of other Parameters:

The present study deals with the two phase system using toluene as solvent. Toluene is comparatively low cost. The reaction highly depends on the properties of organic solvent that affect the transport properties of phase transfer catalyst. For further study, solvent like n-heptane, dodecane, dichloromethane, chlorobenzene can be used. The selection of solvent is essential for the transportation of the immiscible phases. It can transfer the mass from aqueous phase to organic phase.

The study of pH of alkanolamine solution is also important to the formation of ion in the aqueous phase. Selectivity of bis(4-chlorobenzyl) sulfide depends on the S^{2-}/HS^{-} ratio as we studied from the reaction mechanism. This ratio depends on the pH of the alkaline solution. Therefore the work can be tried out by using alkali solution like NaOH and other anions such as co-catalyst that can affect the rate of reaction as well as selectivity of the desired product.

6.2 Investigating the Possibilities of the other fine Chemicals:

Like mercaptan and diaryl sulfide, other the value added chemicals can be examined by using H_2S rich MDEA solution or any other alkanolamine solution. Selective formations of organic sulphides are also important in chemical industry so that they can be formed soluble disulfide or bisulfide by using hazardous H_2S.

6.3 Reusability of PT Catalyst:

Present study based on liquid-liquid PTC which is normally not recovered and recycled. It is considered as a waste. To overcome the problems, liquid-liquid-liquid phase transfer catalyst or any other insoluble catalyst can be tried for environmental benefits. Using the third phase

catalyst, the reaction can be carried out that gives the high yields, purity of the products, increase the reaction rate and it minimized the industrial waste (Yadav et al.2012).

6.4 Searches for Better Catalyst:

For the enhancement of rate of reaction, yield and conversion, we can use another type of catalyst such as surfactant type of catalyst cetyltrimethylammonia bromide (CTMAB), ionic liquid trihexyltetradecyl phosphonium bromide (THTDPB) (Yadav et al. 2010) etc.

6.5 Large –Scale Application of Present Study:

Before applying for large-scale process, the present systems ought to be tried get into a scaled-up to envision out the performance of the presence method. In our study separation and purification of the product haven't been tried out. After carrying out the reaction mixture in large scale, the separation of the liquids can be done by using distillation or other chemical process depending upon on the nature of components. Additionally identification of the products will be done by different technique like nuclear magnetic resonance (NMR), Fourier Transform infrared Spectroscopy (FTIR).

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